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(54) TREATMENT OF POROUS CARBONACEOUS ELECTRODE, CARBONACEOUS FIXED BED TYPE THREE-DIMENSIONAL ELECTRODE ELECTROLYTIC CELL AND TREATMENT OF WATER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a treating method with high removing rate and sterilizing efficiency of bacteria in a carbonaceous fixed bed type three-dimensional electrode electrolytic cell in which bacteria in water is electrochemically treated by passing water through a carbonaceous fixed bed type three-dimensional electrode, by using a porous carbonaceous electrode treated under specified conditions.
SOLUTION: In a carbonaceous fixed bed type three-dimensional electrode electrolytic cell in which water is electrochemically treated by passing water through a carbonaceous fixed bed type three-dimensional electrode, a porous carbonaceous three-dimensional electrode to be used in the electrolytic cell is treated in a water vapor atmosphere at 100 to 130° C. In a carbonaceous fixed bed type three-dimensional electrode electrolytic cell in which bacteria in water is electrochemically treated by passing water through a carbonaceous fixed bed type three-dimensional electrode, a porous carbonaceous electrode treated in a water vapor atmosphere at 100 to 130° C is used for the electrolytic cell.

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CLAIMS

[Claim(s)]
[Claim 1] The art of the porous carbonaceous electrode characterized by processing the porous carbonaceous electrode used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically under a 100-130-degree C steam ambient atmosphere.
[Claim 2] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by the porous carbonaceous electrode used for this cell processing under a 100-130-degree C steam ambient atmosphere in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically.
[Claim 3] The water treatment approach characterized by impressing the 2nd applied voltage which has a reversal period shorter than the reversal period of the 1st electrolytic voltage to the process which the polarity of the 1st electrolytic voltage impressed to a cell reverses in the water treatment approach of reversing the polarity of applied voltage in case a carbonaceous fixed-bed mold three-dimensions electrode cell is passed and processed water is processed electrochemically.
[Claim 4] The water treating unit which has the electrolytic voltage generator which impresses the 2nd applied voltage which has a reversal period shorter than the reversal period of the 1st electrolytic voltage to the process which the 1st electrolytic voltage impressed to a cell inverts in the water treating unit which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode cell, and processes processed water electrochemically.
[Claim 5] the water treatment approach by the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically -- the water treatment approach characterized by being, and adding and processing the halogenide of alkali metal to treated water.
[Claim 6] The water treatment approach characterized by processing the treated water containing the halogenide of 0.005 - 0.5% of alkali metal with a cell in the water treatment approach of passing a carbonaceous fixed-bed mold three-dimensions electrode cell, and processing the processed water in a processing tub electrochemically, and returning this in a processing tub.
[Claim 7] The carbonaceous fixed-bed mold three-dimensions electrode cell used for the water treatment approach according to claim 6 characterized by having two or more through tubes whose apertures are 0.3-3mm in the carbonaceous fixed bed.
[Claim 8] An approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell characterized by to arrange this metal auxiliary electrode so that this metal auxiliary electrode may be contacted in the center of abbreviation of this carbonaceous fixed bed, and to suppress this metal auxiliary-electrode periphery with an elastic body gasket when having been distorted so that the metal auxiliary electrode which touches the carbonaceous fixed bed in an approach to assemble the carbonaceous fixed-bed mold three-dimensions

electrode cell which is made to pass and is processed electrochemically for a carbonaceous fixed-bed mold three-dimensions electrode in processed water may serve as a convex.
[Claim 9] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being assembled by the approach according to claim 8 of assembling.
[Claim 10] In an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically When the metal auxiliary electrode in contact with the carbonaceous fixed bed is distorted irregularly, this metal auxiliary electrode is arranged so that it may contact by the periphery of this carbonaceous fixed bed, and the periphery of this metal auxiliary electrode is an elastic body gasket. The center of abbreviation is an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell characterized by arranging so that it may press down with the spacer separated or it was united with the gasket and this metal auxiliary electrode may become almost parallel to this carbonaceous fixed bed.
[Claim 11] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being assembled by the approach according to claim 10 of assembling.
[Claim 12] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by forming the plate which has micropore in the upstream of the carbonaceous fixed bed by the side of the top style of a cell.
[Claim 13] In the art of the carbonaceous fixed bed used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically This carbonaceous fixed bed arranged so that the carbonaceous fixed bed may constitute a part of wall surface of a tight container and the abbreviation disregard of the leak of the fluid from the clearance between this carbonaceous fixed bed and a tight container can be carried out The art of the carbonaceous fixed bed characterized by taking out the foreign matter in this carbonaceous fixed bed to the exterior by soaking in water or an aquosity solvent, and sending in and pressurizing air or inert gas in a tight container.
[Claim 14] In the equipment which takes out to the exterior the foreign matter in the carbonaceous fixed bed used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically This carbonaceous fixed bed arranged so that the carbonaceous fixed bed may constitute a part of wall surface of a tight container and the abbreviation disregard of the leak of the fluid from the clearance between this carbonaceous fixed bed and a tight container can be carried out Equipment which takes out to the exterior the foreign matter in the carbonaceous fixed bed characterized by soaking in water or an aquosity solvent, and sending in and pressurizing air or inert gas in a tight container.
[Claim 15] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being pressed down by the carbonaceous fixed bed which the electrode for electric supply of the upstream adjoins with an elastic body at least in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode cell, and processes the processed water in a processing tub electrochemically.
[Claim 16] The carbonaceous fixed-bed mold three-dimensions electrode cell according to claim 15 with which the elastic body which presses down the electrode for electric supply of the above-mentioned upstream is characterized by being a flat spring or a compression spring.
[Claim 17] In the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically, while arranging a carbonaceous fixed-bed mold three-dimensions electrode in a heat-resistant container The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by having arranged the heat source for touching the water flow on the street of the upstream, and/or the outside of a cell, and heating the liquid in a cell to 70-100 degrees C rather than a cell in a cell container.
[Claim 18] In the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed

water electrochemically A cell consists of a heat-resistant container and the outside of the heat-resistant container is covered with a heat insulator. Arrange the heat source for heating in a heat-resistant container, and heating to 70-100 degrees C for electrode playback is performed by automatic or manual operation. The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by having the function to adjust the flow rate of processed water so that the flow rate of processed water may become the following during heating by water flow cross-section 0.05l./per two of 1cm of a cell.

[Claim 19] In the water treating unit containing the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically It is. this cell consists of a heat-resistant container, and the means for heating said carbonaceous fixed-bed mold three-dimensions electrode is arranged on a circulation path, and automatic -- being certain -- by manual operation The water with which heating of the 70-100-degree C electrode plate for electrode playback was performed, and it was heated on said circulation path after heat-treatment termination is a water treating unit characterized by having the function which passage is changed and is discharged out of a system.

[Claim 20] In the electrode playback approach of the water treating unit containing the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically It is. this cell consists of a heat-resistant container, and the means for heating said carbonaceous fixed-bed mold three-dimensions electrode is arranged on a circulation path, and automatic -- being certain -- by manual operation For passage, the water with which heating of the 70-100-degree C electrode plate for electrode playback was performed, and it was heated on said circulation path after heat-treatment termination is the electrode playback approach that it is characterized by changing and discharging out of a system.

[Claim 21] The carbonaceous electrode used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically A laminating and two or more compressed fibroid sheets are heat-treated using an organic binder, and they are carbonization and the graphite-ized thing. The carbonaceous electrode which carries out cutting of this molding object, and is characterized by processing it so that the angle of the circulation direction of treated water and the laminating side of said fibroid sheet to make may become 10-80 degrees.

[Claim 22] The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by using a carbonaceous electrode according to claim 21 in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of preventing and recovering the lock out by the foreign matter in collapse of the porous carbonaceous electrode by electrolysis, and treated water, and/or the carbon fines by collapse of an electrode while raising the sterilization effectiveness of the processed water containing a microorganism, and recovery / removal effectiveness of a processed underwater impurity.
[0002]
[Description of the Prior Art] When current and we live, the water of various classes is used. For example, they are well water, tap water, industrial water, pure water, ultrapure water, organ bath water, pool water, etc. Moreover, the used water turns into waste industrial waters or domestic wasted water. Or the water which contains various matter in various industries is used. These water solutions etc. offer nourishment with a moderate solute, or microorganisms, such as bacteria, breed that the solution temperature of this water solution is temperature desirable to propagation, performance degradation, such as said water, is caused or doing various bad influences is known. Moreover, various impurities are contained in industrial liquid waste, and impurity removal for environmental pollution prevention or recovery of the useful matter is performed.
[0003] For example, in paper sensitive-material processing after image exposure, photosensitive material is processed through down stream processing of the color development, bleaching fixing, rinsing, and/or stabilization, and, subsequently it dries. And in such a photographic-processing process, although various photographic-processing liquid, such as color development liquid, bleach liquor, a bleach fix bath, a fixer, slurry, and rinsing water, is used The fault that an irregular color arises on the print obtained while the microorganism mixed into said photographic-processing liquid breeds and reducing the effectiveness of sensitive-material processing, or mold and an image pollutes according to generating etc. has produced said sensitive material in order to offer the environment which contained gelatin content and was suitable for microorganism propagation. Although control of degradation of the photographic-processing liquid by this microorganism propagation has the approach in use of sterilizing said microorganism by the injection of an antifungal agent etc. from the former, and carrying out activation of the engine performance, by this approach, the antifungal agent to add is needed for a large quantity, and this antifungal agent becomes easy to remain in photographic-processing liquid or said sensitive material, and it may have a bad influence on sensitive material. Moreover, if said many of antifungal agents are not in the condition which was hard to be referred to as harmless to the body, and was managed under various regulation systems, the use is difficult for it. Moreover, antibacterial [to that antifungal agent] may also generate the antifungal agent chosen in this way after a while, and the troublesome problem of choosing an antifungal agent to antibacterial [this] again arises.
[0004] Moreover, many microorganisms, such as bacteria harmful to the body, inhabited the water used for a pool, and since this pool water has high possibility of contacting a user's eye, a wound, etc. directly and producing a disease, it disinfected by having fed drugs, such as sodium

hypochlorite, into pool water, and has prevented generating of a disease. However, chlorine-based reagents, such as a strong hypochlorous acid of a bactericidal effect and liquid chlorine, are used as said drugs, and even if itself or a decomposition product has stimulative and effectiveness, such as sterilization, arises with this reagent, side effects with this reagent, such as a pain of an eye and a rash of the skin, occur, and this chlorine-based reagent poses a big problem, when it is the weak small child of especially drag force. Moreover, since the amount of the pool water which cannot carry out permanent use, but needs to continue addition in pool water like every day in order to disassemble a chlorine-based reagent, and is used for a pool is immense, it serves as a burden also with the big cost of the drugs to be used.

[0005] Moreover, the need of various papers, especially quality paper is growing by progress of an information society in recent years. Although these papers are manufactured through various processes from paper pulp, this process that washes the pulp in front of paper manufacture in process, and flushes an unnecessary component exists. Since it is maintained by moderate temperature and moderate nourishment is included, if these mold and bacteria remain in a final product so much that microorganisms, such as mold and bacteria, tend to breed, degradation of engine performance, such as tenebrescence of papers, will produce this pulp. Therefore, an antifungal agent and a germicide contain and he is trying to prevent the performance degradation of a final product as much as possible in the wash water of the immense amount used at this washing process. However, by this approach, there is a trouble that performance degradation other than the performance degradation by which said antifungal agent and germicide remain in a product, and the cost of an antifungal agent or a germicide not only becomes high, but they originate in mold or bacteria may be caused.

[0006] Furthermore, the installation number of the various air conditioning equipments installed in this building etc. is also increasing by leaps and bounds with the increment in buildings, such as a building which the companies of apartments, such as an apartment in recent years, or a large number gather, and is formed. At the apartment and building in which the air conditioning equipment of such a large number is installed, the facility for heat exchangers of the cooling water of this air conditioning equipment, for example, a cooling tower, is usually installed in the roof. When the cooling water of this heat exchanger facility also continues prolonged use, microorganisms, such as mold and bacteria, breed and it deposits in the heat exchange side of said heat exchanger, and the heat exchange engine performance may be worsened, or a microorganism may occur massive and may blockade piping etc. Moreover, the trash of a microorganism generated so much may cause serious problems, such as corrosion, in piping or a device.

[0007] Furthermore, if breed quickly, it is polluted and it becomes impossible for a microorganism to continue use, although the amount of the bathroom water used is increasing from spread and the hot spring boom of a home organ bath in recent years, and leaving it, without using it for bathing since this bathroom water has the solution temperature to which the microorganism around 40 degrees C tends to breed also repeats bathing, the dirt of the body etc. will float and this inclination will become more remarkable. Since the microorganism which bred is minute, by filtration actuation, it is hard to remove, and since the amount used is especially huge in the public bath, if the polluted bathroom water is reproducible by easy processing actuation, a large cost cut will be attained.

[0008] Furthermore, besides the natural fishes which are breeding to the sea or a river as various fishes resources, the farmed fishes in a nursery attract attention and, recently, many farmed fishes are supplied to the commercial scene. Microorganisms contained in inside, such as bacteria and mold, pollute fishes. the time of breeding of these fishes in a nursery -- fish breeding -- service water -- It is added so much to service water. or the various drugs for annihilating the microorganism of all, such as a germicide and an antifungal agent, or most, in order to control the bad influence of adhering to fishes and reducing the commodity value -- said fish breeding -- Furthermore, in order to suppress damage on the fishes by said drugs to the minimum, fishes are medicated with a lot of nutrients, such as a vitamin compound, and food is given on it. Therefore, the fishes which the fishes bred in a nursery etc. had much addition of the various drugs artificially prescribed for the patient as compared with the amount of food and

a vitamin compound, and the antifungal agent and the germicide were accumulated in the inside of the body of fishes, and were polluted with various drugs harmful to the body will be supplied to a commercial scene.
[0009] Furthermore, after potable water carries out disinfection processing of the water which stored water to sources, such as a reservoir, in purification plant, it is supplied to each home, a drink store, etc. through a water supply system. Although said disinfection of potable water has the common processing by chlorine, while disinfection of potable water is performed comparatively good, according to this chlorination, the fault that the mellowness which natural water has for a bleaching powder smell is spoiled produces it.
[0010] There is the approach of processing electrochemically currently indicated by JP,3-224686,A, 4-27488, etc. as a water treatment method without the above faults. According to this approach, a special chemical etc. cannot be used but a lot of water can be processed. However, in these approaches, a method of improving the improvement in processing effectiveness, collapse prevention of a carbon electrode, and lock out is desired.
[0011]
[Problem(s) to be Solved by the Invention] The purpose of this invention is in the approach of processing electrochemically the processed underwater microorganism which uses a fixed-bed mold three-dimensions electrode cell to offer the high fixed-bed mold three-dimensions electrode cell and high art of removal / sterilization effectiveness of a microorganism.
[0012] Furthermore, it aims at offer of the fixed-bed mold three-dimensions electrode cell with which the adhesion of a metal auxiliary electrode and the fixed bed is improved, and collapse by anodic oxidation of an electrode is suppressed.
[0013] Moreover, it aims at offering the approach of improving the lock out by the carbon particle produced by collapse of a processed underwater foreign matter or the carbonaceous fixed bed.
[0014]
[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the following configuration.
[0015] (1) The art of the porous carbonaceous electrode characterized by processing the porous carbonaceous electrode used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically under a 100-130-degree C steam ambient atmosphere.
[0016] (2) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by the porous carbonaceous electrode used for this cell processing under a 100-130-degree C steam ambient atmosphere in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically.
[0017] (3) The water treatment approach characterized by impressing the 2nd applied voltage which has a reversal period shorter than the reversal period of the 1st electrolytic voltage to the process which the polarity of the 1st electrolytic voltage impressed to a cell reverses in the water treatment approach of reversing the polarity of applied voltage in case a carbonaceous fixed-bed mold three-dimensions electrode cell is passed and processed water is processed electrochemically.
[0018] (4) The water treating unit which has the electrolytic voltage generator which impresses the 2nd applied voltage which has a reversal period shorter than the reversal period of the 1st electrolytic voltage to the process which the 1st electrolytic voltage impressed to a cell inverts in the water treating unit which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode cell, and processes processed water electrochemically.
[0019] (5) the water treatment approach by the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically -- the water treatment approach characterized by being, and adding and processing the halogenide of alkali metal to treated water.

[0020] (6) The water treatment approach characterized by processing the treated water containing the halogenide of 0.005 – 0.5% of alkali metal with a cell in the water treatment approach of passing a carbonaceous fixed-bed mold three-dimensions electrode cell, and processing the processed water in a processing tub electrochemically, and returning this in a processing tub.
[0021] (7) The carbonaceous fixed-bed mold three-dimensions electrode cell used for the water treatment approach of said six publications characterized by having two or more through tubes whose apertures are 0.3-3mm in the carbonaceous fixed bed.
[0022] (8) An approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell characterized by to arrange this metal auxiliary electrode so that this metal auxiliary electrode may be contacted in the center of abbreviation of this carbonaceous fixed bed, and to suppress this metal auxiliary-electrode periphery with an elastic body gasket when having been distorted so that the metal auxiliary electrode which touches the carbonaceous fixed bed in an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass and is processed electrochemically for a carbonaceous fixed-bed mold three-dimensions electrode in processed water may serve as a convex.
[0023] (9) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being assembled by the approach assembling said eight publications.
[0024] (10) In an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically When the metal auxiliary electrode in contact with the carbonaceous fixed bed is distorted irregularly, this metal auxiliary electrode is arranged so that it may contact by the periphery of this carbonaceous fixed bed, and the periphery of this metal auxiliary electrode is an elastic body gasket. The center of abbreviation is an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell characterized by arranging so that it may press down with the spacer separated or it was united with the gasket and this metal auxiliary electrode may become almost parallel to this carbonaceous fixed bed.
[0025] (11) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being assembled by the approach assembling said ten publications.
[0026] (12) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by forming the plate which has micropore in the upstream of the carbonaceous fixed bed by the side of the top style of a cell.
[0027] (13) In the art of the carbonaceous fixed bed used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically This carbonaceous fixed bed arranged so that the carbonaceous fixed bed may constitute a part of wall surface of a tight container and the abbreviation disregard of the leak of the fluid from the clearance between this carbonaceous fixed bed and a tight container can be carried out The art of the carbonaceous fixed bed characterized by taking out the foreign matter in this carbonaceous fixed bed to the exterior by soaking in water or an aquosity solvent, and sending in and pressurizing air or inert gas in a tight container.
[0028] (14) In the equipment which takes out to the exterior the foreign matter in the carbonaceous fixed bed used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically This carbonaceous fixed bed arranged so that the carbonaceous fixed bed may constitute a part of wall surface of a tight container and the abbreviation disregard of the leak of the fluid from the clearance between this carbonaceous fixed bed and a tight container can be carried out Equipment which takes out to the exterior the foreign matter in the carbonaceous fixed bed characterized by soaking in water or an aquosity solvent, and sending in and pressurizing air or inert gas in a tight container.
[0029] (15) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by being pressed down by the carbonaceous fixed bed which the electrode for electric supply of the upstream adjoins with an elastic body at least in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-

dimensions electrode cell, and processes the processed water in a processing tub electrochemically.
[0030] (16) The carbonaceous fixed-bed mold three-dimensions electrode cell of said 15 publications with which the elastic body which presses down the electrode for electric supply of the above-mentioned upstream is characterized by being a flat spring or a compression spring.
[0031] (17) In the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically, while arranging a carbonaceous fixed-bed mold three-dimensions electrode in a heat-resistant container The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by having arranged the heat source for touching the water flow on the street of the upstream, and/or the outside of a cell, and heating the liquid in a cell to 70-100 degrees C rather than a cell in a cell container.
[0032] (18) In the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically A cell consists of a heat-resistant container and the outside of the heat-resistant container is covered with a heat insulator. Arrange the heat source for heating in a heat-resistant container, and heating to 70-100 degrees C for electrode playback is performed by automatic or manual operation. The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by having the function to adjust the flow rate of processed water so that the flow rate of processed water may become the following during heating by water flow cross-section 0.05l./per two of 1cm of a cell.
[0033] (19) In the water treating unit containing the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically It is. this cell consists of a heat-resistant container, and the means for heating said carbonaceous fixed-bed mold three-dimensions electrode is arranged on a circulation path, and automatic -- being certain -- by manual operation The water with which heating of the 70-100-degree C electrode plate for electrode playback was performed, and it was heated on said circulation path after heat-treatment termination is a water treating unit characterized by having the function which passage is changed and is discharged out of a system.
[0034] (20) In the electrode playback approach of the water treating unit containing the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically It is. this cell consists of a heat-resistant container, and the means for heating said carbonaceous fixed-bed mold three-dimensions electrode is arranged on a circulation path, and automatic -- being certain -- by manual operation For passage, the water with which heating of the 70-100-degree C electrode plate for electrode playback was performed, and it was heated on said circulation path after heat-treatment termination is the electrode playback approach that it is characterized by changing and discharging out of a system.
[0035] (21) The carbonaceous electrode used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically A laminating and two or more compressed fibroid sheets are heat-treated using an organic binder, and they are carbonization and the graphite-ized thing. The carbonaceous electrode which carries out cutting of this molding object, and is characterized by processing it so that the angle of the circulation direction of treated water and the laminating side of said fibroid sheet to make may become 10-80 degrees.
[0036] (22) The carbonaceous fixed-bed mold three-dimensions electrode cell characterized by using the carbonaceous electrode of said 21 publications in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically.
[0037] This invention is explained to a detail below. the fixed-bed mold three-dimensions electrode cell of this invention -- the flat electrode for electric supply of a pair -- by arranging the fixed bed of the porosity of 3-15 preferably [it is desirable and / one or more] to mesh-like

inter-electrode, and impressing direct current voltage to the electrode for electric supply of the aforementioned pair, polarization of the porosity fixed bed is carried out, and it is removal and the water treating unit to sterilize of microorganisms, such as bacteria, a virus, and protozoa, through treated water at this fixed bed. Or it can use also for recovery of a processed underwater metal component, or electrochemical decomposition removal of an impurity.
[0038] This invention removes and sterilizes a processed underwater microorganism efficiently in the approach of processing electrochemically the processed underwater microorganism which uses a fixed-bed mold three-dimensions electrode cell, by activating a carbonaceous front face by processing the carbonaceous fixed bed to be used under a 100-130-degree C steam ambient atmosphere. That is, when removing a microorganism processed underwater with the carbonaceous fixed-bed mold three-dimensions electrode cell of this invention, a microorganism once sticks to the carbonaceous fixed bed, it is thought that electrolysis processing is carried out and this is sterilized on an electrode, and since it becomes easy to carry out adsorption of a up to [the electrode of a microorganism] by processing of this invention, it is presumed that removal / sterilization effectiveness improved. Although processing of this carbonaceous fixed bed may process only a porous carbon electrode plate, it may be processed as the carbonaceous fixed bed which consists of a porous carbon electrode plate, a metal auxiliary electrode, and a gasket. Or it is also possible to process the whole cell container in the condition of having been arranged in a cell. In this case, it is effective, if it lets water flow in a cell container beforehand and the porous carbon electrode plate is wet with water. This processing can use the commercial autoclave for sterilization. In that case, 120 degrees C, 2atm, and the processing for 20 minutes are desirable. Although this processing is effective also with a new porous carbon electrode plate, remarkable effectiveness is demonstrated to the porous carbon electrode plate with which the adsorption power of a microorganism declined by especially used. It is more effective, if it carries out combining alkali cleaning and/or acid cleaning (for example, it lets 0.05-5N NaOH and 0.05-5N HCl flow, is immersed, and the organic substance and an inorganic substance are removed) when reproducing a used porous carbon electrode plate.
[0039] In the art which reverses the polarity of the electrolytic voltage impressed to a carbonaceous fixed-bed mold three-dimensions electrode cell in case processed water is processed electrochemically, another mode of this invention is an art characterized by impressing the 2nd electrical potential difference with a polarity it being lower than the 1st electrolytic voltage, and reverse, in case the polarity of the 1st electrolytic voltage impressed to a cell is reversed. That is, this is based on the fact that sterilization effectiveness improves, if repetitive reversal of the polarity of electrolytic voltage is carried out. Although the mechanism is not clear, when removing and sterilizing a microorganism processed underwater with a carbonaceous fixed-bed mold three-dimensions electrode cell as mentioned above, a microorganism is made to once adsorb on a carbon electrode, and electrolysis sterilization is carried out. Although the sterilized bacillus has some which exfoliate automatically, it is guessed by carrying out repetitive reversal of the polarity of electrolytic voltage that the bacillus to which it once stuck becomes easy to exfoliate. It is considered by this for a new microorganism to be easy to adsorb on a carbonaceous electrode. Impression of electrolytic voltage is usually reversing the polarity periodically. Since components, such as calcium, Mg, Si, etc. which are contained in processed underwater one, deposit by electrolysis, this has prevented dissolving this again and an electrode and a cell blockading. Usually, the polarity is reversed at intervals of 15 - 60 minutes. In addition to the polarity reversals of the 1st applied voltage for electrolysis processing, in this invention, repetitive reversal of the 2nd applied voltage for electrode playback is performed. Although it was made conventionally reversed with +E1 ->-E1 ->+E1 or -E1 ->+E1 ->-E1 at intervals of 15 - 60 minutes when the 1st applied voltage is set to +E1 or -E1 and the 2nd applied voltage for electrode playback was specifically set to +E2 or -E2 In this invention, the repetitive reversal process of the 2nd applied voltage for electrode playback is added to this. Although the repetitive reversal process of the 2nd applied voltage may be inserted anywhere in the electrical-potential-difference impression process of the 1st applied voltage, it is desirable to insert, in case the polarity of the 1st applied voltage is reversed. That is, it is +E1 ->(-E2 ->+E2) n->-E1 ->(+E2 ->-E2) m->+E1 or +E1 ->-E1 ->(+E2 ->-E2) l->+E1.

[0040] Preferably, +E1 and −E1 are carried out, and abbreviation etc. is, they carry out time amount impression here, and impression time amount is 15 − 60min once. Moreover, as for n, m, or especially l, it is desirable that it is more than the number of the fixed beds of the cell currently used for one or more integers. + Carry out E2 and −E2, and abbreviation etc. is, they carry out time amount impression, and, as for impression time amount, it is desirable that it is [1 time] 5 − 60 seconds. Moreover, although the same electrical potential difference is sufficient as applied voltage E1 and applied voltage E2, a high electrical potential difference lower than applied voltage E1 or is sufficient as applied voltage E2. High sterilization effectiveness came to be acquired over the long period of time by this.
[0041] Another mode of this invention is the approach of adding and processing the halogenide of alkali metal to treated water, in the carbonaceous fixed−bed mold three−dimensions electrode cell which is made to pass a carbonaceous fixed−bed mold three−dimensions electrode, and processes processed water electrochemically. This approach is effective when a lot of organic substance is included in especially processed underwater one. For example, at the processing plant of edible chicken, before packing the chicken which took out internal organs finally, it is washing within the processing tub containing cold water. Since a lot of piece of meats and constituents of blood are contained in such wash water, it is the environment where bacteria tend to breed. Thus, when a lot of organic substance was included in processed underwater one, it became clear by adding and processing the halogenide of alkali metal to treated water that it could sterilize very efficiently. Specifically, NaCl or KCl is added and processed so that it may become processed water with 0.005 − 0.5%. In this case, since a sterilization component with durability, such as a hypochlorous acid, is generated, higher sterilization effectiveness is acquired by the synergistic effect with the above−mentioned sterilization mechanism. Remarkable effectiveness is acquired in case circulation processing in which it is returned to a flush tank or a treated water tub after especially this approach processes water, such as a flush tank or a treated water tub, with this equipment is performed. By preparing two or more through tubes whose apertures are 0.3−3mm in the nature electrode of porous carbon used at this time, the fall of the flow rate at the time of continuous running was controlled, and it became clear that processing effectiveness improves. Although the number of through tubes can be prepared in arbitration, it is desirable for total of the puncturing area of two or more through tubes to be 1 − 10% of the water flow cross section of a carbonaceous electrode.
[0042] By the way, in the carbonaceous fixed−bed mold three−dimensions electrode cell, collapse by anodic oxidation of a carbonaceous electrode poses a problem. In order to prevent this, the carbonaceous electrode was sandwiched with auxiliary electrodes, such as metal, and collapse of a carbon electrode is prevented by mainly generating the oxygen by electrolysis of water on this metal electrode. However, after a metal auxiliary electrode and a metal carbon electrode separated, there was a problem that collapse of a remarkable carbon electrode occurred. Usually, the mesh−like thing is used and, as for the metal auxiliary electrode, that whose thickness is about 1mm is used. Therefore, if it is going to return that it is difficult to return to a flat surface completely once it is distorted [distortion or / which becomes empty] according to external force, and by force, it will be distorted rather unevenly.
[0043] When drawing 2 explains, the carbonaceous fixed−bed mold three−dimensions electrode cell [drawing 2 (g)] of this invention consists of what piled up two or more carbonaceous fixed−bed mold three−dimensions electrodes which sandwiched the porous carbon electrode (carbonaceous fixed bed) 1 by the metal auxiliary electrode 2 and 2', and have wrapped the whole in the gasket 3, as drawing 2 (a) shows. The perspective view of a carbonaceous fixed−bed mold three−dimensions electrode is shown in drawing 2 (b). When normal, as shown in drawing 2 (c), a metal auxiliary electrode is a flat surface and touches by the carbonaceous fixed bed and the whole. However, as mentioned above, when a metal auxiliary electrode was distorted and the bent electrode was used, the part which does not contact a carbon electrode partially arose, and there was a problem that electrode collapse advanced in the part.
[0044] So, an approach to assemble for preventing this is offered in another mode of this invention. That is, in the carbonaceous fixed−bed mold three−dimensions electrode cell which is made to pass a carbonaceous fixed−bed mold three−dimensions electrode, and processes

processed water electrochemically, when the metal auxiliary electrode in contact with the carbonaceous fixed bed is curving, it is an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell which arranges a metal auxiliary electrode so that the carbon electrode which touches as shown in drawing 2 (f) may be contacted in the center of abbreviation of opposite Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. In this case, it is desirable to suppress a periphery with the gasket which consists of an elastic body. When it includes in a cell by carrying out like this, a periphery is suppressed by the gasket, a metal auxiliary electrode and a carbon electrode are stuck mostly, since the periphery is covered by the gasket, polarization is suppressed and there is also still less effect of anodic oxidation.
[0045] Another is an approach to assemble the carbonaceous fixed-bed mold three-dimensions electrode cell which arranges a metal auxiliary electrode so that a metal auxiliary electrode may be contacted in a carbon electrode by the periphery of opposite Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne., as shown in drawing 2 (d) or (e). In this case, the spacer separated or it was united with the gasket in the center of abbreviation between the metal auxiliary electrodes with which it adjoins in a cell is formed. When the force was added in the water flow direction between each carbon electrode and a metal auxiliary electrode through a gasket and/or a spacer by doing in this way, each was able to contact exactly, could prevent collapse of the carbon electrode by anodic oxidation, and was able to reduce consumption of an electrode.
[0046] Moreover, it became clear that the upstream face of the carbon electrode arranged most at the upstream tends to collapse rather than other carbon electrodes of the downstream by operation of a prolonged cell. Therefore, in order to solve this problem, as a result of inquiring wholeheartedly, it found out solving by forming the plate which has micropore in the upstream of the fixed bed by the side of the top style of a cell. As shown in drawing 10 (b), specifically, the porous plate has been arranged by water flow nature between the carbon electrodes contiguous to the outside of the electrode for electric supply, or the electrode for electric supply. A porous plate has glass, a ceramic, resin, fiber, a desirable nonwoven fabric, etc., and, as for thickness, the thing of 50-200 micrometers of average apertures is preferably used by 0.5-5mm. The problem that the carbon electrode most arranged by this at the upstream tends to collapse rather than others was solved.
[0047] Moreover, in another mode of this invention, the approach except foreign matters, such as carbon fines in a porous carbonaceous electrode, is offered. That is, in the carbon electrode used for the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode, and processes processed water electrochemically, it became clear that an internal foreign matter and carbon fines could be removed efficiently by sending air into the electrode plate wet beforehand. In the cylinder 14 which specifically has a larger bore than the outer diameter of the carbonaceous fixed-bed mold three-dimensions electrode 17 or the porous carbon electrode (carbonaceous fixed bed) 1 as shown in drawing 3 (a) When a carbon electrode is soaked in water or an aquosity solvent as leak of the fluid of the part of the clearance between the lateral portion of a carbonaceous electrode and a cylinder is prevented, and one side inserts this in the cylinder of the abbreviation closing **** above in the abbreviation level condition with the lid 15 of an elastic body It is the approach of taking out the foreign matter in the carbonaceous fixed bed to the exterior. Like drawing 3 (a), with a piston 16, the porous carbon electrode 1 set to the upper part is pushed caudad, and is taken down to drawing 3 (b). Foreign matters, such as carbon fines in the porous carbon-electrode 1 interior, blow off up like an arrow head with the pressure of the air into which the lower part was compressed. You may push by hand instead of a piston 16, and another carbonaceous fixed-bed mold three-dimensions electrode 17 may be installed in a cylinder instead of the lid 15 of an elastic body, and abbreviation seal space may be formed.
[0048] Or it arranges so that the carbonaceous fixed-bed mold three-dimensions electrode 17 or the porous carbon electrode (carbonaceous fixed bed) 1 may constitute some wall surfaces of a tight container, and it arranges using a gasket etc. so that the abbreviation disregard of the leak of the fluid from the clearance between this carbon-electrode lateral portion or an edge, and a tight container can be carried out. In this case, since the compressed air is sent from the downward air induction inlet 19 as drawing 4 (a) shows, the base material 18 is installed in the

tight container so that the porous carbon electrode 1 may not shift. Water or an aquosity solvent is put into the field of the upper part (outside of airtight space) of the porous carbon electrode 1, and an electrode is wet, or the electrode is wet beforehand. Then, the foreign matter in a carbon electrode is taken out by sending in and pressurizing air or inert gas in a tight container outside. If water or an aquosity solvent is stored in the upper part, since a foreign matter will come out in this water or an aquosity solvent, this water or an aquosity solvent is discarded together with a foreign matter. like drawing 4 (a), although one sheet is sufficient at a time as this processing, it is shown in drawing 4 (c) -- as -- many -- several sheets are sufficient. In drawing 4 (c), the ring-like spacer 9 is used so that the carbonaceous fixed-bed mold three-dimensions electrode 17 may not contact, respectively and water supply wastewater can be performed smoothly.

[0049] Moreover, although they are abbreviation identitas, as shown in drawing 4 (b), if a principle and a configuration spray water and a penetrant remover on the tight container inside or dip the tight container outside in water or a penetrant remover conversely at the same time they send in and pressurize air in a tight container, they are effective [they are the point of an atomizer about water or a penetrant remover, and].

[0050] By the way, since the carbonaceous fixed bed would move by water pressure to the downstream if processed water is returned to a carbonaceous fixed-bed mold three-dimensions electrode cell with the water pressure of 2kg/cm2 or more, in order that spacing or carbonaceous electrode, and metal auxiliary electrode of the electrode for electric supply and the carbonaceous fixed bed might separate, there was a problem that collapse of the carbon electrode by anodic oxidation broke out. So, in another mode of this invention, this problem was solvable with the cell characterized by being pressed down by the carbonaceous fixed bed which the electrode for electric supply of the upstream adjoins with an elastic body at least in the carbonaceous fixed-bed mold three-dimensions electrode cell which is made to pass a carbonaceous fixed-bed mold three-dimensions electrode cell, and processes the processed water in a processing tub electrochemically. As shown in drawing 5 (b) or (e), specifically, a spring can also be used as some wiring to the electrode for electric supply as the metal spring 21 or metal flat-spring 21'. When using flat-spring 21', and plate spring geometry has the small diameter of a cell, as shown in drawing 11 (a), the flat spring of only one side is sufficient, but if the diameter of a cell becomes large, spring pressure will also make many number of feather high like drawing 11 (b) and drawing 11 (c). It is arbitrary, and plate spring geometry is good and its number of feather is also arbitrary. Moreover, although a flat spring is metal, titanium is desirable and the titanium by which platinum plating was carried out is the most desirable.

[0051] The configuration of the carbonaceous fixed-bed mold three-dimensions electrode cell which used metal flat-spring 21' for drawing 12 (a), and used the compression spring 41 for it at drawing 12 (b) is shown. Although the exploded view of the lower part of drawing 12 (b) is shown in drawing 13 , a compression spring 41 is inserted in the metal rod 39 welded to the core of electrode 4', and it supports with the metal electric conduction rod 40. Since the power from the outside is given to electrode 4' with the electric conduction rod 40 and the metal rod 39, a compression spring 41 may not have a thing with conductivity, either.

[0052] Furthermore, it is also possible to make wiring to the electrode for electric supply into a wire separately like drawing 5 (a) using the spring 20 which used non-conductive materials, such as resin. Or as shown in drawing 5 (c), the elastic bodies 22, such as rubber of the shape of a globular shape and a column, can also be used.

[0053] Moreover, the cell of this invention had the problem that the sterilization engine performance fell gradually, when operation was continued by prolonged continuation. Then, in order to solve this problem, as a result of continuing examination wholeheartedly, it became clear by heat-treating a cell periodically that the sterilization engine performance is reproduced. Although the reason is not clarified, it is surmised that it is because the adsorption power of the bacillus to the carbon electrode to which it fell by continuous running is reproduced. The cell of this invention consists of a container which consists of heat-resistant materials, such as polycarbonate resin or Teflon resin. Heat-resistant high materials also of the gasket and spacer to be used, such as EPDM (ethylene propylene rubber), are also desirable. For example, as shown in drawing 6 , in the cell, the heater 24 is installed as a heating means. This heater 24 is

energized from the outside with lead wire 25, and is heated. Moreover, as for a cell, it is desirable to cover the outside with the heat insulator 23. Whenever [stoving temperature] is 70 degrees C or more, and if it processes for 10 - 30 minutes preferably above 70 degrees C for several minutes to 1 hour, it is effective.

[0054] As for these heating means, being prepared in the upstream of a cell is desirable, and the flow rate of the treated water in a cell is wanted to be the following by zero thru/or water flow cross-section 0.05l./per two of 1cm during heat-treatment. Electrolysis can stop during heat-treatment. As for the heated water which is discharged from a cell during heat-treatment or after processing termination, it is desirable to change passage so that it may be discharged by the excretory system.

[0055] Furthermore, it is desirable to install a heat source in the circulatory system, as shown in drawing 7 (a), and to heat-treat not only processing of a cell but all filter and piping. In drawing 7 (a), a measurement system is a broken line, a dotted line shows a control system and it shows the automatic-control circulation system. Although it is introduced from the water feed hopper 27 and accumulated in the circulating water tub 28, if a signal goes into a control device from a liquid level sensor 29 and the water to process becomes a predetermined amount, it will close a bulb 31 and will stop supply of water. The water included in the circulating water tub 28 is bottled through a flowmeter 32, after water treatment is introduced and carried out to the body 26 of a cell through the method cock 30 of three, a pump 35, and the filter 34 of 33 or 10 micrometers of pressure gages. If the sterilization engine performance falls and it comes to repeat circulation many times, a heater 24 will be turned ON and it will be introduced into the body 26 of a cell through the method cock 30 of three, a pump 35, and the filter 34 of 33 or 10 micrometers of pressure gages from the circulating water tub 28, but as amount of water was mentioned above, it is made below by water flow cross-section 0.05l./per two of 1cm, and water is heated by 70 degrees C or more. The water which passed the cell operates the method cock 30 of three, is led to the wastewater section, and is discharged outside. Or the whole system can also be heat-treated, the method cock 30 of three is moved so that treated water may pass along a bulb 31, and as water circulates through the path between bottling water and wastewater, the heat-treated water is circulated within a system. A flow rate is increased by 0.05l./after heat-treatment termination above (desirable usually 50 - 100% of flow rate at the time of operation), and after draining fixed time amount (for example, for 1 - 30 minutes) to an excretory system, it can change passage and can usually return to operation. These actuation can control the change of a bulb, the drive of a pump, ON/OFF of a heater, etc. by the control device automatically.

[0056] Moreover, a heater is installed in the auxiliary tank 36 of Rhine like drawing 7 (b), water can be returned to a cell and the treated water heated here can also be processed. Furthermore, the acid for washing, alkali, etc. can be added in the auxiliary tank 36, circulation supply of this can also be carried out into a system, and it can also carry out to coincidence apart from heat treatment. In addition, in drawing 7 (b), since it was the same, illustration of Rhine of the servomechanism shown by drawing 7 (a) and a control system, and a measurement system was omitted.

[0057] The cell of this invention can be heat-treated with hand control or automatic to the timing of the arbitration under operation. It is spacing set up beforehand preferably, for example, it is desirable to be automatically heat-treated at intervals of one day - one month.

[0058] The carbonaceous fixed-bed mold bipolar type cell of this invention is a carbonaceous fixed-bed mold bipolar type cell which prevented easily balking of two or more of said carbonaceous fixed beds from said tube-like object by installing a base material in a part of opening of the lower part of a tube-like object which holds two or more carbonaceous fixed beds. This carbonaceous fixed-bed mold bipolar type cell concerning this invention is applicable to metal ion recovery of reforming processing of processed water, the complex ion in a water solution, etc.

[0059] photographic-processing liquid, potable water, pool water, the cooling water for heat exchangers, bathroom water, and fish breeding -- by processing processed water, such as service water, with the cell concerning this invention, reforming, such as processed water

sterilization, is performed and complex ion is collected from this solution whose processed water is a low concentration complex ion content solution as metal silver.
[0060] Moreover, by the cell of this invention, sterilization of microorganisms, such as processed underwater one, bacteria (bacteria), mold (mold), yeast, slime mould, unicellular algae, protozoa, and a virus, is performed, and the water quality is improved.
[0061] That is, if processed water is supplied to a carbonaceous fixed-bed mold three-dimensions electrode cell, a this processed underwater microorganism will be considered that contacted and adsorb in the carbonaceous fixed bed of said cell, the electrode terminal for electric supply, etc., receive a powerful oxidation reduction reaction on those front faces, or contact the electrode of high potential, the weak relaxation itself becomes [the activity] extinct, and sterilization is performed by liquid flow.
[0062] In using this cell for reforming processing of processed water +0.2--+1.2V without oxygen evolution with substantial anode potential for impression potential (vs.S C E), Although it is desirable to make it cathode potential substantially set to 0--1.0V (vs.S C E) without hydrogen generating, when the matter in liquid does not receive an oxidation reduction reaction and change of acidity or alkalinity does not arise, or when the reacting weight does not become a problem so much again, higher anode potential can be impressed. For example, the mesh electrode spacing made from titanium which prepares the mesh electrode made from titanium with a thickness of 1mm which carried out platinum plating in the both sides of a porous carbonaceous electrode with a thickness of 9mm, and adjoins these respectively in piles eight steps can be set to 1mm, and, in the case of the cell which set to 1mm spacing of the mesh electrode made from titanium of both ends piled up eight sheets, and the electrode for electric supply, the electrical potential difference of 20-50V can be impressed to this electrode for electric supply. When it considers as a 11-step pile on the same conditions, the electrical potential difference of 30-70V can be impressed to this electrode for electric supply. When using a **** cell as objects for metal recovery, such as silver metallurgy, reduction of a metal ion should just impress sufficient potential to be generated on an electrode.
[0063] If the generation of gas follows [in the case of reforming of processed water] especially in extensive processing like pool water or paper manufacture wash water Hydrogen gas, the occurring gas, i.e., the oxygen gas, is usually generated in the mixing ratio within the explosion limit. In order to avoid the risk of explosion, diluting with inert gas, such as air, is desirable, for example, a means to dilute so that the separation means of the electrolysis gas which occurs to a cell outlet, and this electrolysis gas after separation may be diluted with air and electrolysis gas concentration may become below 4 capacity % can be installed.
[0064] It is advantageous at the point which use of the carbonaceous fixed-bed mold bipolar type cell of large this invention of a throughput is desirable, can be immense as for the amount of water which should be processed in the case of processed water, such as pool water, for example, a touch area with the processed water which should be processed by use of this cell can be increased, and can make equipment size small by this since it becomes several t per hour, and can gather the effectiveness of electrochemical processing.
[0065] Generally the electrode in the fixed-bed mold three-dimensions electrode cell of this invention can choose this nature fixed-bed mold three-dimensions electrode from carbon system ingredients, such as the activated carbon and the graphite which have a configuration according to the cell which the above-mentioned uses, and have configurations, such as the shape of the shape of the porous material which can penetrate said processed water, for example, a grain, a globular shape, and felt, and textile fabrics, and a letter of a porosity block, and a carbon fiber, including a carbonaceous fixed-bed mold three-dimensions electrode and the electrode for electric supply preferably.
[0066] The carbonaceous fixed bed of this invention has desirable porous carbon graphite of 20-100 micrometers of average apertures. These are the porous carbon electrode plates which were heat-treated and carbonized, heat-treated further, two or more sheets made from a vegetable fiber, for example, Japanese paper etc., etc. which carried out the laminating for example, using the organic substance binder, and graphite-ized it at the temperature of 1000 degrees C or more in the inert gas ambient atmosphere. More preferably, since there are also few impurities about

two or more sheets made from a synthetic fiber using an organic substance binder and a laminating and the porous carbon electrode plate which pressed, heat-treats this, was made to carbonize, heat-treated further, and was graphite-ized are easy also for control of a pore diameter, it is desirable. Since the width of face of pore diameter distribution becomes Sharp narrowly especially to the target pore diameter, blinding stops being able to happen easily. Especially although phenol resin, an epoxy resin, etc. can be used for the organic substance binder used for such an application, it is not limited to these. Although what was woven to blanket-like is sufficient as the sheet made from a synthetic fiber, a non-woven fabric is sufficient. Since the major axis of fiber is extended in the longitudinal direction, as for the carbon electrode which calcinated cloth or paper after the laminating and the press, and created it, water tends to flow in the direction in which fiber is extended. Although the electrode plate which is easy to let flow by processing it so that the direction of a major axis of fiber and the circulation direction of unsettled water may be made in agreement is obtained in case an electrode plate is created, it is easy to exfoliate between the layers which carried out the laminating in case of this, and the problem that flexural strength falls arises. Therefore, the direction of fiber also becomes slanting by processing it so that the include angle with the pressed field to make may become aslant (10-80 degrees preferably 30-60 degrees C) to the circulation direction of the unsettled water in an electrode plate. Water flow resistance can obtain an electrode plate also with few [it is few and] falls of flexural strength which cannot carry out blinding easily by using such an electrode plate.

[0067] Namely, since the major axis of fiber is extended in the longitudinal direction (on a laminating side) as the conventional carbon electrode is shown in drawing 8 (a), water tends to flow in the direction in which fiber is extended. In case an electrode plate is created, as shown in drawing 8 (b), the electrode plate which is easy to let flow by processing it so that the direction of a major axis of fiber and the circulation direction of unsettled water may be made in agreement is obtained, but since it is easy to exfoliate between the layers which carried out the laminating, the problem that flexural strength falls arises. Therefore, in order to solve this problem, as a result of repeating examination wholeheartedly, as shown in drawing 8 (c), the direction of fiber also becomes slanting by processing it so that the include angle alpha of the circulation direction of the unsettled water in an electrode plate and the laminating side of fiber to make may become aslant (10-80 degrees preferably 30-60 degrees C). Water flow resistance was able to obtain the electrode plate also with few [it is few and] falls of flexural strength which cannot carry out blinding easily by using such an electrode plate.

[0068] These carbon-electrode plates can also arrange two or more sheets in one gasket. For example, one porous graphite of 50 micrometers of 9mm apertures in thickness is sufficient, and three things of 50 micrometers of 3mm apertures in thickness may be used in piles. Furthermore, it can also change into arbitration, for example, 100 micrometers of apertures can be sandwiched in the center, they can sandwich porous graphite of 50 micrometers of apertures on those both sides, and an aperture and thickness can be installed, and can also use as the one fixed bed this thing piled up three sheets.

[0069] The carbonaceous fixed bed of these plurality by which the laminating was carried out is held in the tube-like object in which vertical both ends carry out opening. As for this tube-like object, it is desirable to form with the electrical insulation material which can be equal also to prolonged use or use for the second time, and the polyepichlorohydrin which is especially synthetic resin, polyvinyl methacrylate, polyethylene, polypropylene, a polyvinyl chloride, the Pori ethylene chloride, phenol-formaldehyde resin, ABS plastics, acrylic resin, a polycarbonate, etc. can be used for it. Furthermore, if it fabricates with transparence or a translucent ingredient, since the condition [exhausting] of said carbonaceous fixed bed can be checked by looking, it is convenient.

[0070] An EQC, since that diameter is a minor diameter a little, when it grasps only this tube-like object and operates exchange of said carbonaceous fixed bed etc. rather than the bore of said tube-like object, this carbonaceous fixed bed secedes from downward opening, and it becomes impossible for said two or more carbonaceous fixed beds held in this tube-like object to hold the carbonaceous fixed bed of a predetermined number in a tube-like object.

[0071] Therefore, it is desirable to install a base material and to prevent balking of said carbonaceous fixed bed, i.e., the fall from a tube-like object etc., so that a part of lower part of said tube-like object or upside opening may be blockaded in the cell concerning this invention. Especially if the configuration of this base material has only the reinforcement which controls migration of two or more of said carbonaceous fixed beds, it will not be limited. A doughnut-like object so that this doughnut-like object may plug up a part of opening in the lower limit section of said tube-like object fix by welding, adhesion, etc. or Or, and it can fix by adhesion etc. or a reticulum can be similarly installed in said embarrassment circles so that the periphery part of the lower limit of a tube-like object may be straddled in the member of a cross-joint mold. [really casting the member of the same configuration as this] Moreover, a screw can be engraved on said DONATSU-like object and tube-like object, the screw stop of both the members can be carried out, and it can also fix mutually. Moreover, the upper part of opening can install a base material by the screw stop similarly, and can hold said carbonaceous fixed bed in said tube-like object in the more stable condition from these.
[0072] In addition, if balking from the tube-like object of this base material according that it is desirable carrying out to 3 - 50% of the opening area of opening, and it is less than 3% to the lack of on the strength becomes easy to produce the vertical cross section in the flow direction of the processed water of this base material and 50% is exceeded to it, while checking circulation of processed water, it becomes easy to cause the rise of electrolytic voltage.
[0073] This carbonaceous fixed bed is placed into a direct current or alternating current electric field. Direct current voltage or alternating voltage is impressed between the electrode terminals for electric supply which consist of perforated plate objects, such as the shape of the shape of plate-like or an expanded mesh installed in both ends, or a par FERE Ted plate. It is possible to carry out polarization of said carbonaceous fixed bed, and to consider as the carbonaceous fixed-bed mold bipolar type cell which held the three-dimensions electrode which is made to form an anode plate and cathode in the end and the other end of this carbonaceous fixed bed according to polarization, respectively, and grows into them. In addition, it can install, and it can connect electrically and can consider as a carbonaceous fixed-bed mold bipolar type cell so that the three-dimensions ingredient which functions as cathode as an anode plate independently may not be short-circuited by turns.
[0074] as the quality of the material of said anode plate terminal for electric supply -- for example, carbon graphite material (a carbon fiber --) GURASHI carbon, such as a carbon cross and graphite, a graphite composite (what mixed and sintered the metal by powder to carbon), To an activated carbon fiber nonwoven fabric (for example, KE-1000 felt and Toyobo (Co., Ltd.)) or this, platinum, There are an ingredient which made palladium, nickel, etc. support, and the quality of the material further formed from a dimensionally stable electrode (platinum group oxide covering titanium material), platinum covering titanium material, nickel material, stainless steel material, iron material, etc. The cathode terminal for electric supply which counters the anode plate terminal for **** electric supply, and gives negative direct current voltage can be formed from the metallic material which covered platinum, stainless steel, titanium, nickel, copper, Hastelloy, graphite, carbon material, annealed copper, or a platinum metal.
[0075] In processing processed water, generating oxygen gas from an anode plate as said carbonaceous fixed bed using carbon system ingredients, such as activated carbon, graphite, and a carbon fiber, said carbonaceous fixed bed oxidizes with oxygen gas, and it becomes easy to dissolve it as carbon dioxide gas. In order to prevent this, the porous material or reticulated ingredient which covers platinum metal oxides, such as oxidization iridium and ruthenium oxide, and is used for the side in which said carbonaceous fixed bed carries out positive polarization as an auxiliary electrode on base materials, such as titanium, is installed in the state of contact, and to make it oxygen evolution arise mainly on this ingredient is desired. It can also be used for them, being able to stick electrically carbon material (0.5-2.0mm in thickness), such as glassy carbon which has two or more phi0.1-3mm pores for water flow instead of the auxiliary electrode using said metal so that surface hole density may become 10 - 80%, to carbon electrodes, such as said porous carbon graphite.
[0076] Since the processing effectiveness of processed water will fall if the opening where liquid

can circulate, without contacting a carbonaceous electrode material is in the cell with which the processed water which should be processed flows, it is important for the carbonaceous fixed bed etc. to arrange so that the flow of the processed water in a cell may not carry out a short pass. Therefore, this leak style can be prevented by covering the periphery and lateral portion of a carbonaceous electrode material with one gasket. The example in the case of assembling such a cell is shown. That is, the fixed bed which built the carbonaceous electrode material and the metal auxiliary electrode into the gasket beforehand is produced. Since it is made of the material with the resiliency of rubber etc., when the gasket is produced a little more smallish than the dressed size of a carbonaceous electrode material or a metal auxiliary electrode and is inserted in with enlargement, it is desirable in respect of adhesion. Moreover, in order that the gasket of the lateral portion of a carbonaceous electrode material may prevent leaking from breadth and here with the water pressure at the time of water flow, it is desirable to prepare the projection of a little larger outer diameter than the container bore which holds the fixed bed. Moreover, you may also insert a metal auxiliary electrode with a carbonaceous electrode material, and it may be attached on a carbonaceous electrode material.

[0077] There is also the approach of filling up the clearance between an electrode and a cell container with resin for the above-mentioned leak prevention. Thermosetting resin, a silicon sealant, etc. are used for such resin. Or an electrode plate may be put in heat-shrinkable tubing, and may be heat-treated. However, once it hardens by resin, there is a fault of decomposition becoming less easy.

[0078] It is also possible to paste up an auxiliary electrode and a carbon electrode with conductive resin, and it is effective in order to control collapse of the carbon electrode by anodic oxidation.

[0079] Moreover, when these cells used the carbonaceous electrode material which the problem of a lifting or a cone for blinding had, therefore opened in the processed water inflow side of a carbonaceous electrode material the hole of two or more not penetrating, for the carbon impalpable powder produced by the processed underwater foreign matter or anodic oxidation, it became clear that the blinding by the foreign matter or the carbon particle was controlled remarkably. As for the depth of a hole, 1/4 to 3/4 of a carbonaceous electrode material is desirable, and 0.5-4.0mm of an aperture is desirable. 5 - 25% of the carbonaceous electrode material of the area of the part of a hole is desirable.

[0080] Moreover, since there is little lateral migration and the contact of the flow rate of the processed water supplied to said cell on a carbonaceous fixed-bed front face decreases that it is a perfect laminar flow, it is desirable to form a turbulent flow condition and especially the thing to consider as the turbulent flow which has the 500 or more Reynolds numbers is [that what is necessary is just to specify that this processed water can contact front faces, such as an electrode, efficiently] desirable [a flow rate].

[0081] The cell which consists of such a configuration processes by connecting with the part or all the tubs of a photographic-processing process, such as a color development tub, a bleaching tub, a bleaching fixing tub, a rinsing process tub, and a stabilization process tub, and supplying and circulating through the photographic-processing liquid in said each processing tub to said cell, when using it as an object for sterilization of the microorganism for example, in photographic-processing liquid. Moreover, also when using it as an object for the silver recovery from photographic-processing liquid, a photographic-processing tub is made to approach similarly and it installs, and it can energize supplying the fixer containing complex ion etc. to said cell, and silver can be collected.

[0082] Furthermore, the heat exchanger by which the cell of this invention was installed in a building, the roof of an apartment, etc., Or a pool or a paper maker is further installed in office bathrooms and organ baths for home use, such as a faucet of reservoir Rhine of purification plant, such as a nursery and a fishing pond, or the waterworks of a home or a restaurant or a public bath, and a hot spring. By introducing each processed water into said cell, and processing it electrochemically, reforming processing of sterilization of said processed water etc. can be performed.

[0083] In addition, in the cell of this invention, the leakage current arises in this cell, and this

leakage current flows into other members, for example, photographic-processing tub, through processed water, such as photographic-processing liquid, from a cell. Since induction of the electrochemical reaction which is not desirable may be carried out in this photographic-processing tub, or the wall surface of a photographic-processing tub is made to corrode electrochemically and elution of the wall surface component may be carried out, In entrance piping of the electrode tooth-back section which the positive-negative pole in a cell does not face, and/or said cell, from said processed liquid, a conductive high member can be installed so that touch-down of the end may be possible, and said leakage current can be intercepted. This is effective also to other processed water.

[0084] Next, although the desirable example of the carbonaceous fixed-bed mold three-dimensions electrode cell concerning this invention is explained based on an accompanying drawing, the cell of this invention is not limited to this cell.

[0085] In each drawing, the laminating of the carbonaceous fixed bed 1 of a porous carbon graphite electrode is carried out, and the carbonaceous fixed bed is sandwiched by the metal auxiliary electrode (for example, titanium mesh by which platinum plating was carried out) 2, and 2'. The carbonaceous fixed bed and an auxiliary electrode are held by the gasket (for example, product made of rubber) 3 with elasticity, and are stuck to the inside of a cell. By returning water to processed water by the pressure of 0.5 - 5 kgf/cm2 from the entry (IN) of a cell, and applying an electrical potential difference to an electrode 4 and 4' from the exterior, processed water is sterilized and is taken out from upside (OUT).

[0086] Drawing 1 is the sectional view of a comparative carbonaceous fixed-bed mold three-dimensions electrode cell. the processed water introduced from the upside entry (IN) -- the tooth space 7 (processed water installation way) between the container liners 5 and outer cases 6 of a cell -- a passage -- the inside of an electrode -- passing -- OUT -- reaching . In case processed water passes according to an arrow head, power is supplied from an electrode 4 and 4' through the electrode terminal 11 from the outside, and 11', and in case it passes through the metal auxiliary electrode 2 and the carbonaceous fixed-bed carbon electrode 1 inserted into 2', recovery of sterilization of the bacteria contained in processed underwater one or silver is performed. Since the laminating of the carbonaceous fixed bed is pinched and carried out to the metal auxiliary electrode 2 and 2', it continues and polarizes in the upper part from the lower part. Each carbonaceous fixed bed 1 and metal electrode 2, and 2' are blocked by the gasket 3 so that processed water may not leak from a flank. The top cover 10 and the outer case 6 are assembled with the screw so that these groups may be set. The air-vent plug 12 is formed so that processed water may be smoothly introduced into the water omission plug 13 and the beginning which discharge internal water in the case of washing.

[0087]

[Example] Next, although this invention is explained based on an example, the embodiment of this invention is not limited to this.

[0088] Example 1 synthetic fiber was used as the aggregate, and it piled up with the organic substance binder, and cast by the pressure of 200 kgf/cm2, this molding was heat-treated, and porous carbon graphite with a thickness of 9mm was created. It was 51 micrometers in 60% of porosity, and average pore diameter. It considered as the porous carbon electrode of a comparison of this. Furthermore, this porous carbon graphite was wet with water, with the autoclave, 2 atm, 20min processing was carried out and 120 degrees C of porous carbon electrodes of this invention were obtained.

[0089] The cell shown in drawing 1 was created only using the porous carbon electrode of this invention. Moreover, the cell was similarly created using the comparative porous carbon electrode.

[0090] The fixed bed is 76mm in the thickness of 9mm, and diameter in porous carbon graphite.

[0091] Said porous carbon graphite was sandwiched using the titanium mesh (thickness of 1mm) covered with platinum as a metal auxiliary electrode. Direct-current 34V were impressed to this cell at the electrode terminal for electric supply, and the polarity was reversed at intervals of 30 minutes. In the case of this cell, an electrical potential difference can be changed into arbitration in 20-50V.

[0092] A sterilization performance test is Pseudomonas. After cultivating diminuta for one day using the liquid medium (a nutrient broth culture medium, EIKEN CHEMICAL make) and carrying out centrifugal separation of the fungus body in 5000rpm, pure water washed and centrifugal separation was carried out again. It added to the tap water (residual chlorine concentration is 0.01 ppm or less) which accumulated this beforehand, and considered as processed water. This was returned to the cell using the porous carbon electrode of this invention, and the cell using a comparative porous carbon electrode by the pressure of 1.2kg/cm2, the processed water before and behind cell passage was bottled, and the number of micro organisms contained in this was measured with the agar plate process using a nutrient agar medium (EIKEN CHEMICAL make). The result is shown in Table 1. Two kinds from which the number of micro organisms differs, and 1 and 2 were used for processed water. The rate of sterilization was computed from the following formula.

[0093]

[Equation 1]

$$\text{制菌率（\%）} = \left(1 - \frac{\text{電解槽通過後の処理水中の生菌数（CFU／mℓ）}}{\text{電解槽通過前の処理水中の生菌数（CFU／mℓ）}}\right) \times 100$$

[0094]

[Table 1]

	被処理水	生菌数測定結果(CFU/mℓ)		制菌効率%
		IN側	OUT側	
本発明の電解槽	1	8.6×10^4	8.3×10^1	99.9%
	2	3.1×10^3	1.2×10^1	99.6%
比較の電解槽	1	8.2×10^4	1.1×10^4	86.6%
	2	3.5×10^3	5.6×10^2	84%

[0095] From Table 1, it became clear that the direction of the cell using the porous carbon electrode of this invention was clearly excellent in sterilization effectiveness.

[0096] The same cell as the cell of the comparison used in the example 2 example 1 was prepared. The electrical potential difference of the pattern respectively shown in the following table 2 was repeated and impressed to these electrodes for electric supply.

[0097]

[Table 2]

	電　圧　印　加　方　法
比較の電圧印加方法	40v(15min)→－40v(15min)→40v(15min)
本発明の電圧印加方法－1	40v(15min)→－40v(15min)→(40v(15sec)→－40v(15sec))8→40v(15min)
本発明の電圧印加方法－2	40v(15min)→－40v(15min)→(25v(30sec)→－25v(30sec))8→40v(15min)

[0098] About each electrical-potential-difference impression approach, the sterilization engine performance was compared by the following approach. It is Pseudomonas with the same approach as an example 1. It adjusted each 20l. of processed water containing diminuta (about 105 CFU(s)/ml), and prepared for the tank. With the equipment shown in drawing 9 , this processed water was returned to the cell of a comparison of an example 1 by the 2l. pressure for /, the processed water after cell passage was again returned to the tank, and repetition processing was performed. The processed water in a tank was bottled the time of processing initiation, and 3 hours after processing initiation, and the number of micro organisms contained in this was measured with the agar plate process using a nutrient agar medium (EIKEN CHEMICAL make). The result is shown in Table 3.

[0099]

[Table 3]

	開始時の生菌数	3時間後の生菌数
比較の電圧印加方法	3×10^{5}CFU／ml	2×10^{3}CFU／ml
本発明の電圧印加方法－1	3×10^{5}CFU／ml	5×10^{1}CFU／ml
本発明の電圧印加方法－2	3×10^{5}CFU／ml	1×10^{2}CFU／ml

[0100] It was checked that the electrical-potential-difference impression approach of this invention is excellent in the sterilization engine performance from Table 3.

[0101] The same cell as the cell of the comparison used in the example 3 example 1 was prepared, and these were installed as a cell of the circulation processing system shown in drawing 9 , respectively.

[0102] A sterilization performance test is Escherichia. After cultivating coli for 16 hours using the liquid medium (a nutrient broth culture medium, EIKEN CHEMICAL make) and carrying out centrifugal separation of the fungus body in 5000rpm, pure water washed and centrifugal separation was carried out again. It added to the tap water (residual chlorine concentration is 0.01 ppm or less) which accumulated this beforehand, NaCl of further different concentration was added, and it considered as processed water.

[0103] 20l. of this processed water was put into the circulating water tub 28 shown in drawing 9 , respectively. 34V were impressed to the cell, the polarity was reversed every 15 minutes, and the pump performed circulation processing for 30 minutes by the flow rate of 1l. / min. The

processed water before processing and after processing was bottled, and the number of micro organisms contained was measured using the DESOKISHIKO rate agar medium (EIKEN CHEMICAL make). The case where the example 41 of a comparison and alkali halide are added for the case where nothing is added to processed water is made into the examples 41-43 of this invention, and a result is shown in Table 4.

[0104]

[Table 4]

		処理前の生菌数	循環処理後の生菌数
比較例41	0% NaCl	2×10^5CFU/ml	5×10^1CFU/ml
本発明例41	0.01% NaCl	2×10^5CFU/ml	0 CFU/ml
本発明例42	0.1% NaCl	2×10^5CFU/ml	0 CFU/ml
本発明例43	0.05% KCl	2×10^5CFU/ml	0 CFU/ml

[0105] It was checked that the art of the processed water of this invention is excellent in the sterilization engine performance from Table 4.

[0106] The through tube (phi1mm and 3mm) was prepared in the porous carbon graphite porosity carbon electrode of example 4 example 1, and two cells which consist of porous carbon graphite which has each through tube were created. The cell was created using the porous carbon electrode of the comparison without a hole, and the circulation processing system as shown in drawing 9 was prepared.

[0107] It is Pseudomonas with the same approach as an example 1. The processed water containing diminuta (about 104 CFU(s)/ml) was adjusted, it added so that it might become 0.04% about NaCl at this, and this was prepared for the tank 30l. This processed water was returned by the 3l. flow rate for /for every cell, the processed water after cell passage was again returned to the tank, and repetition processing was performed. The flow rate of the time of processing initiation and one week of processing initiation, and two weeks after (water is returned with the water pressure of 1.2kg/cm2) and the number of micro organisms of the processed water in a tank were measured with the agar plate process using a nutrient agar medium (EIKEN CHEMICAL make). The result of the examples 51 and 52 of this invention using the cell which consists of porous carbon graphite which has a through tube (the example 51 of a comparison, 52 andphi1mm, and 3mm) using a cell using a porous carbon electrode without a hole is shown in Table 5.

[0108]

[Table 5]

	ポーラスカーボングラファイトの貫通孔の数（1枚あたり）	被処理水に添加したNaCl濃度	生菌数 CFU/ml			流量 リットル/min		
			開始	7日後	14日後	開始	7日後	14日後
比較例51	なし	0%	10^4	10^2	10^2	3.9	3.6	3.2
比較例52	なし	0.04%	10^4	<10	<10	3.9	3.7	3.4
本発明例51	Φ1mm×150コ	0.04%	10^4	<10	<10	4.8	4.8	4.7
本発明例52	Φ3mm×50コ	0.04%	10^4	<10	<10	5.4	5.4	5.3

[0109] After circulation initiation, when all residual chlorine was measured with the portable residual chlorine analyzer (hack company make), in the example 51 of a comparison, it was 0.04 ppm, and was 0.6 ppm in the example 52 of a comparison. It is 1.8 ppm in Example 52 of 2 ppm and this invention in the example 51 of this invention, and the rise of concentration was accepted in a short time after a start up.

[0110] By carrying out circulation processing of the processed water which added the halogenide of alkali metal with the cell which has the through tube of this invention, the fall of the flow rate at the time of continuous running was controlled, and it became clear that processing

effectiveness improves.
[0111] The metal auxiliary electrode shown in example 5 drawing 2 (f) or (e), a carbon electrode and a gasket, or the carbonaceous fixed bed that consists of a spacer further was assembled, the cell shown in drawing 2 (g) using this was created, and it was referred to as the cell (61) of this invention, and (62). Moreover, the cell which assembled the bent metal auxiliary electrode as shown in drawing 2 (d), a carbon electrode and a gasket, or the carbonaceous fixed bed that consists of a spacer further, and was shown in drawing 1 using this was created, and it considered as the comparative cell (61). Moreover, the cell (61) which assembled the metal auxiliary electrode which does not have distortion substantially as shown in drawing 2 (c) as an example of reference, a carbon electrode and a gasket, or the carbonaceous fixed bed that consists of a spacer further, and was shown in drawing 1 using this was created, and this was made into the example of reference. The following carbon electrodes and metal auxiliary electrodes were used for these cells.
[0112] carbon-electrode: -- the cell of each polarity reversals was installed like drawing 9 every 1mm electrolytic condition:DC50V and 30min between the porous carbon graphite phi76mmx thickness of 9mm, the average pore diameter of 60 micrometers, eight porosity 65% metal auxiliary-electrode:platinum covering titanium mesh thickness 1mm cell:carbon electrodes, and a pole, 50l. (300microS [/cm] electrical conductivity) of tap water was prepared for the tank, water was returned with the water pressure of 1.2 kgf/cm2 with the pump, and electrolysis was performed for 96 hours. The anodic oxidation decay rate of a carbon electrode made the index weight percentage reduction after 72-hour electrolysis. Each result is shown in Table 6 as a corresponding example.
[0113]
[Table 6]

	比較例61	参考例61	本発明例61	本発明例62
重量減少率	0.5%	0.2%	0.2%	0.2%

[0114] Thus, even if it used the curved auxiliary electrode, it was checked that the cell built by the approach to assemble this invention is excellent in collapse by anodic oxidation of a carbon electrode few.
[0115] The cell shown in example 6 drawing 10 (a) was made into the example 71 of a comparison, as shown in drawing 10 (b), the porosity plate 37 with a 50 micrometer thickness [of average apertures] of 3mm was formed in this at the upstream of a carbon electrode, and this was made into the cell of the example 71 of this invention. The following carbon electrodes and metal auxiliary electrodes were used for these cells.
[0116] Carbon electrode : The porous carbon graphite phi76mmx thickness of 9mm, The average pore diameter of 50 micrometers, 61% metal auxiliary-electrode:thickness [platinum covering titanium mesh] the cell of 1mm of porosity : Eight carbon electrodes, 1mm electrolytic condition between poles: -- the cell of each polarity reversals was installed in the circulatory system like drawing 9 every DC50V and 30min, 30l. (electrical conductivity S/cm of 310micro) of tap water was prepared for the tank, water was returned with the water pressure of 1.2 kgf/cm2 with the pump, and electrolysis was performed for 96 hours. The anodic oxidation decay rate of a carbon electrode made the index weight percentage reduction of the carbon electrode by the side of the top style after 72-hour electrolysis. The result is shown in Table 7.
[0117]
[Table 7]

	比較例71	本発明例71
最も上流側の炭素電極の重量減少率	0.6%	0.2%
中段の炭素電極の重量減少率	0.2%	0.2%

[0118] Thus, it was checked that collapse by anodic oxidation of the carbon electrode of the upstream is most excellent in the cell of this invention few.

[0119] The cell of the comparison used in the example 7 example 1 and the same cell were prepared, and the circulatory system shown in drawing 9 was constructed. The following were used for the carbon electrode.
[0120] Carbon electrode: The electrical potential difference was impressed to the porous carbon graphite phi76mmx thickness of 9mm, the average pore diameter of 42 micrometers, and 60% cell of porosity by the electrical-potential-difference impression approach of a comparison of an example 2.
[0121] 20l. of tap water was prepared for the tank. This processed water was returned by the 2l. flow rate for /, the processed water after cell passage was again returned to the tank, and repetition processing was performed. The cell was disassembled after carrying out circulation processing for three weeks. After decomposition, the stream washed for 15 minutes, and foreign matters, such as carbon fines which came out from the carbon electrode at this time, were extracted, the weight of the extracted foreign matter was measured, and it considered as the example 81 of a comparison.
[0122] It pushed into the cylinder of the equipment shown in drawing 3 where this carbon electrode is wet, and as shown in drawing 3 , the internal foreign matter was taken out by pushing a piston 16 and sending in air in a [drawing 3 (a) -> drawing 3 (b)] carbon electrode. This actuation was made into the example 81 of repeat this invention 10 times.
[0123] By setting in the equipment shown in drawing 4 (a) as another actuation, and sending in air in a carbon electrode for 10 minutes, the internal foreign matter was taken out and it considered as the example 82 of this invention. Furthermore, the flow rate when assembling a cell again with the electrode after washing, and returning water by 1.2 kgf/cm2 was measured, respectively. The flow rate when assembling a cell again with the weight per carbon electrode of the foreign matter extracted by each approach in Table 8 and the electrode after washing, and returning water by 1.2 kgf/cm2 was shown.
[0124]
[Table 8]

	異物の重量 (g)	流　量 (リットル/min)
比較例81 (流水洗浄)	0.011	1.7
本発明例81 (図3の装置を使用)	0.018	2.0
本発明例82 (図4 (a) の装置を使用)	0.021	2.0

[0125] The example 81 of this invention or 82 is effective in removal of the foreign matter in an electrode, and it was checked that lock out of an electrode is improved by this and a flow rate is improved.
[0126] The cell shown in example 8 drawing 5 (a) and drawing 5 (e) was prepared. That is, the electrode for electric supply of the upstream is supported by means of a spring, and is stuck to an adjoining carbon electrode. This was made into the cell of this invention, respectively. Moreover, the cell shown in drawing 5 (d) was made into the example of a comparison.
[0127] The following carbon-electrode ****** auxiliary electrodes were used for these cells.
[0128] Carbon electrode : The porous carbon graphite phi76mmx thickness of 9mm, The average pore diameter of 51 micrometers, 60% metal auxiliary-electrode:thickness [platinum covering titanium mesh] the cell of 1mm of porosity : Eight carbon electrodes, 1mm electrolytic condition between poles: -- the cell of each polarity reversals was installed like drawing 9 every DC45V and 30min, 30l. (electrical conductivity S/cm of 310micro) of tap water was prepared for the circulating water tub 28, water was returned with the water pressure of 2.8 kgf/cm2 with the pump, and electrolysis was performed for one week. The anodic oxidation decay rate of a carbon electrode made the index most weight percentage reduction of the carbon electrode of the upstream. The result is shown in Table 9.
[0129]
[Table 9]

	最も上流側の炭素電極の重量減少率
比較例91	0.7%
本発明例91	0.4%
本発明例92	0.4%

[0130] Thus, it was checked that collapse by anodic oxidation of the carbon electrode of the upstream is most excellent in the cell of this invention few.
[0131] The cell shown in drawing 6 was assembled as a cell of example 9 this invention, and the circulation system shown in drawing 7 (a) was constructed. The cell of drawing 1 was built into the circulation system of drawing 9 , and this was made into the example of a comparison.
[0132] It is Pseudomonas with the same approach as an example 1. diminuta (about 105 CFU (s)/ml) It adjusted each 50l. of included processed water, and prepared for the tank. This processed water was returned to the cell of this invention by the pressure of 1.2 kgf/cm2, the processed water after cell passage was again returned to the tank, and repetition processing was performed. Heat-treatment shown in the following table 10 the time of processing initiation and day by day [processing initiation 3] was carried out.
[0133]
[Table 10]

	通常運転	加熱工程	洗浄工程	通常運転
流量 (リットル/min)	3	0～0.05	0.1→3	3
排出先	循環水槽	排水	排水	循環水槽
電解電圧	34V	0V	34V	34V
ヒーター	OFF	ON	OFF	OFF
電解槽温度	25℃	25→90℃ (70℃以上で15min)	85→25℃	25℃
処理時間	3日間	25min	5min	3日間

[0134] The sterilization performance test of the cell of this invention was performed by the approach of an example 1 one month after the start up.
[0135] Similarly, processed water was returned to the comparative cell by the pressure of 1.2 kgf/cm2, the processed water after cell passage was again returned to the tank, and repetition processing was performed. The sterilization performance test of the cell of a comparison one month after a start up was performed by the approach of an example 1.
[0136] The result is shown in Table 11.
[0137]
[Table 11]

	制菌率
比較例111	86%
本発明例111	99%

[0138] Thus, as for the cell which gave the cell and the playback approach of this invention, it was checked that the high sterilization engine performance is maintained over a long period of time.
[0139] Using the porous carbon graphite (include angle of alpha= 60 degrees) of example 10 drawing 8 (c), the cell of drawing 1 was assembled and it considered as the cell of this invention. Moreover, using the porous carbon graphite of drawing 8 (a), the cell of drawing 1 was assembled and it considered as the comparative cell.
[0140] The following were used for the carbon electrode.

[0141] carbon-electrode: -- the sterilization engine performance was examined by the approach of an example 1 using the cell of each polarity reversals every the porous carbon graphite phi76mmx thickness of 9mm, average pore diameter of 42 micrometers, porosity 61% metal auxiliary-electrode:platinum covering titanium mesh thickness 1mm electrolytic condition:DC40V, and 30min. Furthermore, the circulatory system shown in drawing 9 was constructed, water was returned with the water pressure of 1.2kg/cm2, continuous running was performed for one month, and the flow rate in the meantime was measured. The result is shown in Table 12.
[0142]
[Table 12]

	制菌率%	流量循環開始時	流量1ヶ月後
比較例121	93%	3.5リットル/min	2.4リットル/min
本発明例121	96%	3.9リットル/min	3.6リットル/min

[0143] It was checked that the cell using the carbon electrode of this invention is excellent in the sterilization engine performance, and the flow rate fall is also excellent few.
[0144]
[Effect of the Invention] By this invention, in the approach of processing electrochemically the processed underwater microorganism using a carbonaceous fixed-bed mold three-dimensions electrode cell etc., it excelled in sterilization effectiveness and the flow rate fall was able to offer few cells and arts.

[Translation done.]

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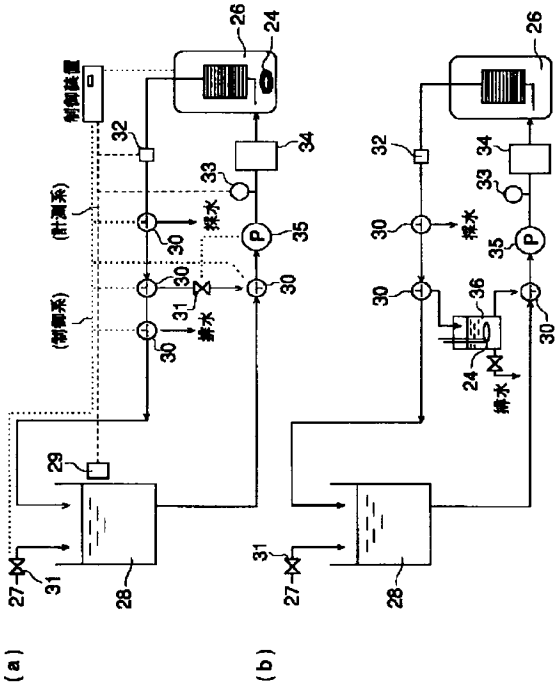
(54)【発明の名称】　多孔性炭素質電極の処理方法、炭素質固定床型三次元電極電解槽及び水処理方法

(57)【要約】

【課題】　炭素質固定床型三次元電極電解槽を用いる被処理水中の微生物等を電気化学的に処理する方法において、制菌効率に優れ、流量低下が少ない電解槽及び処理方法の提供。

【解決手段】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、該電解槽に用いられる多孔性炭素質電極が１００～１３０℃の水蒸気雰囲気下で処理したものであることを特徴とする炭素質固定床型三次元電極電解槽及び該電解槽を用いた水処理方法。



1

【特許請求の範囲】

【請求項１】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いる多孔性炭素質電極を、１００～１３０℃の水蒸気雰囲気下で処理することを特徴とする多孔性炭素質電極の処理方法。

【請求項２】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、該電解槽に用いられる多孔性炭素質電極が１００～１３０℃の水蒸気雰囲気下で処理したものであることを特徴とする炭素質固定床型三次元電極電解槽。

【請求項３】　被処理水を炭素質固定床型三次元電極電解槽を通過させて、電気化学的に処理する際に印加電圧の極性を反転させる水処理方法において、電解槽に印加する第１の電解電圧の極性が反転する工程に、第１の電解電圧の反転周期より短い反転周期を有する第２の印加電圧を印加することを特徴とする水処理方法。

【請求項４】　被処理水を炭素質固定床型三次元電極電解槽を通過させて、電気化学的に処理する水処理装置において、電解槽に印加する第１の電解電圧の極性反転する過程に、第１の電解電圧の反転周期より短い反転周期を有する第２の印加電圧を印加する電解電圧発生装置を有する水処理装置。

【請求項５】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽による水処理方法おいて、処理水にアルカリ金属のハロゲン化物を添加して処理することを特徴とする水処理方法。

【請求項６】　処理槽内の被処理水を炭素質固定床型三次元電極電解槽を通過させて電気化学的に処理する水処理方法において、０．００５～０．５％のアルカリ金属のハロゲン化物を含有する処理水を電解槽で処理し、これを処理槽内に戻すことを特徴とする水処理方法。

【請求項７】　炭素質固定床に孔径が０．３～３ｍｍの複数の貫通孔を有することを特徴とする請求項６記載の水処理方法に用いる炭素質固定床型三次元電極電解槽。

【請求項８】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽の組み立て方法において、炭素質固定床に接触している金属製補助電極が凸となるように歪んでいる場合、該金属製補助電極を該炭素質固定床の略中央で接触するように該金属製補助電極を配置し、該金属製補助電極周辺部を弾性体ガスケットで押さえつけることを特徴とする炭素質固定床型三次元電極電解槽の組み立て方法。

【請求項９】　請求項８記載の組み立て方法により組み立てられたことを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１０】　被処理水を炭素質固定床型三次元電極

2

を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽の組み立て方法において、炭素質固定床に接触している金属製補助電極が不規則に歪んでいる場合、該金属製補助電極を、該炭素質固定床の周辺部で接触するように配置し、該金属製補助電極の周辺部は弾性体ガスケットで、略中央はガスケットと一体となった或いは分離したスペーサーで押さえつけ、該金属製補助電極が該炭素質固定床に対し、ほぼ平行になるよう配置することを特徴とする炭素質固定床型三次元電極電解槽の組み立て方法。

【請求項１１】　請求項１０記載の組み立て方法により組み立てられたことを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１２】　電解槽の最も上流側の炭素質固定床の上流側に微細孔を有する板を設けたことを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１３】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質固定床の処理方法において、炭素質固定床が気密容器の壁面の一部を構成し、かつ、該炭素質固定床と気密容器との隙間からの流体のリークが略無視できるように配置された該炭素質固定床を、水又は水性溶媒で濡らし、気密容器内に空気又は不活性ガスを送り込み加圧することにより該炭素質固定床内の異物を外部へ取り出すことを特徴とする炭素質固定床の処理方法。

【請求項１４】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質固定床内の異物を外部へ取り出す装置において、炭素質固定床が気密容器の壁面の一部を構成し、かつ、該炭素質固定床と気密容器との隙間からの流体のリークが略無視できるように配置された該炭素質固定床を、水又は水性溶媒で濡らし、気密容器内に空気又は不活性ガスを送り込み加圧することを特徴とする炭素質固定床内の異物を外部へ取り出す装置。

【請求項１５】　処理槽内の被処理水を炭素質固定床型三次元電極電解槽を通過させて電気化学的に処理する炭素質固定床型三次元電極電解槽において、少なくとも上流側の給電用電極が弾性体で隣接する炭素質固定床に押さえつけられていることを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１６】　上記上流側の給電用電極を押さえつける弾性体が、板バネ又は圧縮コイルバネであることを特徴とする請求項１５記載の炭素質固定床型三次元電極電解槽。

【請求項１７】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、耐熱性容器内に炭素質固定床型三次元電極を配置するとともに、電解槽容器内、及び

／又は電解槽よりも上流側の通水路上、及び／又は電解槽の外側に接して、電解槽内の液体を７０～１００℃へ加熱するための熱源を配置したことを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１８】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、電解槽が耐熱性容器からなり、その耐熱性容器の外側を断熱材で被覆し、耐熱性容器内に加熱用熱源を配置し、自動もしくは手動操作で電極再生のための７０～１００℃への加熱が行われ、加熱中、被処理水の流量が電解槽の通水断面積１ｃｍ^{2}あたり０．０５リットル／分以下となるように被処理水の流量を調節する機能を有することを特徴とする炭素質固定床型三次元電極電解槽。

【請求項１９】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽を含む水処理装置において、該電解槽が耐熱性容器からなり、前記炭素質固定床型三次元電極を加熱するための手段を循環経路上に配置し、自動的あるい手動操作で、電極再生のための７０～１００℃への電極板の加熱が行われ、加熱処理終了後に、前記循環経路上の加熱された水は流路が切り替えられて系外に排出する機能を有することを特徴とする水処理装置。

【請求項２０】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽を含む水処理装置の電極再生方法において、該電解槽が耐熱性容器からなり、前記炭素質固定床型三次元電極を加熱するための手段を循環経路上に配置し、自動的あるい手動操作で、電極再生のための７０～１００℃への電極板の加熱が行われ、加熱処理終了後に、前記循環経路上の加熱された水は流路が切り替えられて系外に排出することを特徴とする電極再生方法。

【請求項２１】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質電極が、有機質バインダーを使用して積層・圧縮した複数の繊維性シートを熱処理し、炭化及びグラファイト化したもので、この成型体を切削加工して、処理水の流通方向と前記繊維性シートの積層面とのなす角が１０～８０°となるように加工したことを特徴とする炭素質電極。

【請求項２２】　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、請求項２１記載の炭素質電極を使用することを特徴とする炭素質固定床型三次元電極電解槽。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は微生物を含有する被処理水の殺菌効率及び被処理水中の不純物の回収・除去効率を向上させるとともに、電解による多孔性炭素質電極の崩壊及び処理水中の異物及び／又は電極の崩壊による炭素微粉による閉塞を防止・回復する方法に関する。

【０００２】

【従来の技術】現在、我々が生活をする上で様々な種類の水が使用されている。例えば、井戸水、水道水、工業用水、純水、超純水、浴槽水、プール水などである。又、使用された水は工業排水或いは生活排水となる。或いは、各種産業においていろいろな物質を含有する水が利用されている。これらの水溶液等は溶質が適度な養分を提供し、或いは該水溶液の液温が繁殖に好ましい温度であると、細菌等の微生物が繁殖し、前記水等の性能劣化を起こしたり、様々な悪影響を及ぼすことが知られている。また、工場排水などには様々な不純物が含まれており、環境汚染防止のための不純物除去或いは有用物質の回収が行われている。

【０００３】例えば写真感光材料は画像露光の後、ペーパー感光材料処理の場合は、発色現像、漂白定着、水洗及び／又は安定化の処理工程を経て処理され次いで乾燥される。そしてこのような写真処理工程においては、発色現像液、漂白液、漂白定着液、定着液、安定液、水洗水等の各種写真処理液が使用されているが、前記感光材料はゼラチン質を含有し微生物繁殖に適した環境を提供するため、前記写真処理液中に混入した微生物が繁殖して感光材料処理の効率を低下させるとともに得られるプリントに色むらが生じたり黴発生等により画像が汚染するという欠点が生じている。この微生物繁殖による写真処理液の劣化の抑制は、従来から防黴剤の投入等により前記微生物を殺菌して性能を賦活する方法が主流であるが、この方法では添加する防黴剤が多量に必要となり、かつ該防黴剤が写真処理液や前記感光材料中に残留し易くなり、感光材料に悪影響を及ぼすことがある。又前記防黴剤の多くは人体に対して無害とは言い難く、種々の法規制の下に管理された状態でなければその使用が困難である。又このように選択した防黴剤も暫くするとその防黴剤に対する抗菌が発生することがあり、再度この抗菌に対して防黴剤を選択するという煩わしい問題が生ずる。

【０００４】また、プールに使用される水には人体に有害な細菌類等の微生物が数多く生息し、該プール水は利用者の眼や傷などに直接接触して疾患を生じさせる可能性が高いため、プール水には次亜塩素酸ソーダ等の薬剤を投入して消毒を行って疾患の発生を防止している。しかしながら前記薬剤として殺菌効果の強い次亜塩素酸や液体塩素等の塩素系試薬が使用され、該塩素系試薬はそれ自体或いは分解物が刺激性を有し、該試薬により殺菌等の効果が生じても、該試薬による眼の痛みや皮膚のかぶれ等の副作用が発生し、特に抵抗力の弱い幼児の場合は大きな問題となっている。又塩素系試薬は分解するため永続使用することが出来ず毎日のようにプール水に添加を続ける必要があり、かつプールに使用されるプール

水の量は莫大なものであるため、使用する薬剤のコストも大きな負担となっている。

【０００５】また近年の情報化社会の進展により各種紙類特に高質紙の需要が増大している。この紙類は製紙用パルプから各種工程を経て製造されるが、この工程中に製紙前のパルプを洗浄して不要な成分を洗い流す工程がある。該パルプは適度な温度に維持されかつ適度な養分を含むため、黴や細菌等の微生物が繁殖し易くこの黴や細菌が多量に最終製品中に残存すると、紙類の褪色等の性能の劣化が生ずる。従ってこの洗浄工程で使用される莫大な量の洗浄水中には、防黴剤や殺菌剤が含有され最終製品の性能劣化を極力防止するようにしている。しかしこの方法では、防黴剤や殺菌剤のコストが高くなるだけでなく前記防黴剤や殺菌剤が製品中に残存して黴や細菌類に起因する性能劣化とは別の性能劣化を来すことがあるという問題点がある。

【０００６】更に近年におけるマンション等の集合住宅或いは多数の企業が集合して形成されるビル等の建築物の増加に伴い、該建築物等に設置される各種冷暖房設備の設置台数も飛躍的に増加している。このような多数の冷暖房設備が設置されているマンションやビル等では、通常該冷暖房設備の冷却水の熱交換器用設備例えばクーリングタワーがその屋上に設置されている。この熱交換器設備の冷却水も長期間使用を継続すると黴や細菌類等の微生物が繁殖し前記熱交換器の熱交換面に析出して熱交換性能を悪化させたり、微生物が塊状に発生して配管等を閉塞することもある。又多量に発生する微生物の廃棄物により配管や機器に腐食等の重大な問題を引き起こすことがある。

【０００７】更に近年の家庭用浴槽の普及や温泉ブームから浴場水の使用量が増大しているが、該浴場水は４０℃前後の微生物が最も繁殖し易い液温を有するため、入浴に使用せずに単に放置しておくだけでも微生物が急速に繁殖して汚染され、使用を継続出来なくなり、入浴を繰り返すと人体の垢等が浮遊してこの傾向はより顕著になる。繁殖した微生物は微小であるため濾過操作では除去しにくく、特に銭湯などではその使用量が膨大であるため、汚染された浴場水の再生を簡単な処理操作で行うことが出来れば大幅なコストダウンが可能になる。

【０００８】更に各種魚類資源として海や川に繁殖している天然の魚類の他に最近では養殖場における養殖魚類が注目され、養殖魚が市場に数多く供給されている。養殖場におけるこれら魚類の飼育の際には、養魚用水中に含まれる細菌や黴等の微生物が魚類を汚染し、或いは魚類に付着してその商品価値を低下させる等の悪影響を抑制するために殺菌剤や防黴剤等の全部又は大部分の微生物を死滅させるための各種薬剤が前記養魚用水へ多量に添加され、更に前記薬剤による魚類の損傷を最小限に抑えるためにビタミン剤等の多量の栄養剤が魚類に投与され、その上に餌が与えられる。従って養殖場等で飼育される魚類は餌の量に比較して人工的に投与される各種薬剤、ビタミン剤の添加が多く、防黴剤や殺菌剤が魚類の体内に蓄積して人体に有害な各種薬剤で汚染された魚類が市場に供給されることになる。

【０００９】更に飲料水は、貯水池等の水源に貯水された水を浄水場で消毒処理した後、各家庭や飲料店等に上水道を通して供給される。飲料水の前記消毒は塩素による処理が一般的であるが、該塩素処理によると飲料水の消毒は比較的良好に行われる反面、カルキ臭のために天然の水の有するまろやかさが損なわれるという欠点が生ずる。

【００１０】以上のような欠点のない、水処理法として、例えば、特開平３－２２４６８６号、同４－２７４８８号等に開示されている、電気化学的に処理する方法がある。この方法によると、特殊な薬品等を使わず、大量の水を処理することができる。しかし、これらの方法において、処理効率の向上及び炭素電極の崩壊防止及び閉塞を改善する方法が望まれている。

【００１１】

【発明が解決しようとする課題】本発明の目的は、固定床型三次元電極電解槽を用いる被処理水中の微生物を電気化学的に処理する方法において、微生物の除去・殺菌効率の高い固定床型三次元電極電解槽及び処理方法を提供することにある。

【００１２】更に、金属補助電極と固定床との密着性を改善し、かつ電極の陽極酸化による崩壊が抑えられる固定床型三次元電極電解槽の提供を目的とする。

【００１３】また、被処理水中の異物或いは炭素質固定床の崩壊によって生じる炭素微粒子による閉塞を改善する方法を提供することを目的としている。

【００１４】

【課題を解決するための手段】本発明の上記目的は、下記構成により達成された。

【００１５】（１）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いる多孔性炭素質電極を、１００～１３０℃の水蒸気雰囲気下で処理することを特徴とする多孔性炭素質電極の処理方法。

【００１６】（２）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、該電解槽に用いられる多孔性炭素質電極が１００～１３０℃の水蒸気雰囲気下で処理したものであることを特徴とする炭素質固定床型三次元電極電解槽。

【００１７】（３）　被処理水を炭素質固定床型三次元電極電解槽を通過させて、電気化学的に処理する際に印加電圧の極性を反転させる水処理方法において、電解槽に印加する第１の電解電圧の極性が反転する工程に、第１の電解電圧の反転周期より短い反転周期を有する第２の印加電圧を印加することを特徴とする水処理方法。

【００１８】（４）　被処理水を炭素質固定床型三次元電極電解槽を通過させて、電気化学的に処理する水処理装置において、電解槽に印加する第１の電解電圧の極性反転する過程に、第１の電解電圧の反転周期より短い反転周期を有する第２の印加電圧を印加する電解電圧発生装置を有する水処理装置。

【００１９】（５）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽による水処理方法おいて、処理水にアルカリ金属のハロゲン化物を添加して処理することを特徴とする水処理方法。

【００２０】（６）　処理槽内の被処理水を炭素質固定床型三次元電極電解槽を通過させて電気化学的に処理する水処理方法において、０．００５～０．５％のアルカリ金属のハロゲン化物を含有する処理水を電解槽で処理し、これを処理槽内に戻すことを特徴とする水処理方法。

【００２１】（７）　炭素質固定床に孔径が０．３～３ｍｍの複数の貫通孔を有することを特徴とする前記６記載の水処理方法に用いる炭素質固定床型三次元電極電解槽。

【００２２】（８）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽の組み立て方法において、炭素質固定床に接触している金属製補助電極が凸となるように歪んでいる場合、該金属製補助電極を該炭素質固定床の略中央で接触するように該金属製補助電極を配置し、該金属製補助電極周辺部を弾性体ガスケットで押さえつけることを特徴とする炭素質固定床型三次元電極電解槽の組み立て方法。

【００２３】（９）　前記８記載の組み立て方法により組み立てられたことを特徴とする炭素質固定床型三次元電極電解槽。

【００２４】（１０）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽の組み立て方法において、炭素質固定床に接触している金属製補助電極が不規則に歪んでいる場合、該金属製補助電極を、該炭素質固定床の周辺部で接触するように配置し、該金属製補助電極の周辺部は弾性体ガスケットで、略中央はガスケットと一体となった或いは分離したスペーサーで押さえつけ、該金属製補助電極が該炭素質固定床に対し、ほぼ平行になるよう配置することを特徴とする炭素質固定床型三次元電極電解槽の組み立て方法。

【００２５】（１１）　前記１０記載の組み立て方法により組み立てられたことを特徴とする炭素質固定床型三次元電極電解槽。

【００２６】（１２）　電解槽の最も上流側の炭素質固定床の上流側に微細孔を有する板を設けたことを特徴とする炭素質固定床型三次元電極電解槽。

【００２７】（１３）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質固定床の処理方法において、炭素質固定床が気密容器の壁面の一部を構成し、かつ、該炭素質固定床と気密容器との隙間からの流体のリークが略無視できるように配置された該炭素質固定床を、水又は水性溶媒で濡らし、気密容器内に空気又は不活性ガスを送り込み加圧することにより該炭素質固定床内の異物を外部へ取り出すことを特徴とする炭素質固定床の処理方法。

【００２８】（１４）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質固定床内の異物を外部へ取り出す装置において、炭素質固定床が気密容器の壁面の一部を構成し、かつ、該炭素質固定床と気密容器との隙間からの流体のリークが略無視できるように配置された該炭素質固定床を、水又は水性溶媒で濡らし、気密容器内に空気又は不活性ガスを送り込み加圧することを特徴とする炭素質固定床内の異物を外部へ取り出す装置。

【００２９】（１５）　処理槽内の被処理水を炭素質固定床型三次元電極電解槽を通過させて電気化学的に処理する炭素質固定床型三次元電極電解槽において、少なくとも上流側の給電用電極が弾性体で隣接する炭素質固定床に押さえつけられていることを特徴とする炭素質固定床型三次元電極電解槽。

【００３０】（１６）　上記上流側の給電用電極を押さえつける弾性体が、板バネ又は圧縮コイルバネであることを特徴とする前記１５記載の炭素質固定床型三次元電極電解槽。

【００３１】（１７）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、耐熱性容器内に炭素質固定床型三次元電極を配置するとともに、電解槽容器内、及び／又は電解槽よりも上流側の通水路上、及び／又は電解槽の外側に接して、電解槽内の液体を７０～１００℃へ加熱するための熱源を配置したことを特徴とする炭素質固定床型三次元電極電解槽。

【００３２】（１８）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、電解槽が耐熱性容器からなり、その耐熱性容器の外側を断熱材で被覆し、耐熱性容器内に加熱用熱源を配置し、自動もしくは手動操作で電極再生のための７０～１００℃への加熱が行われ、加熱中、被処理水の流量が電解槽の通水断面積１ｃｍ^{2}あたり０．０５リットル／分以下となるように被処理水の流量を調節する機能を有することを特徴とする炭素質固定床型三次元電極電解槽。

【００３３】（１９）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定

床型三次元電極電解槽を含む水処理装置において、該電解槽が耐熱性容器からなり、前記炭素質固定床型三次元電極を加熱するための手段を循環経路上に配置し、自動的あるい手動操作で、電極再生のための７０～１００℃への電極板の加熱が行われ、加熱処理終了後に、前記循環経路上の加熱された水は流路が切り替えられて系外に排出する機能を有することを特徴とする水処理装置。

【００３４】（２０）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽を含む水処理装置の電極再生方法において、該電解槽が耐熱性容器からなり、前記炭素質固定床型三次元電極を加熱するための手段を循環経路上に配置し、自動的あるい手動操作で、電極再生のための７０～１００℃への電極板の加熱が行われ、加熱処理終了後に、前記循環経路上の加熱された水は流路が切り替えられて系外に排出することを特徴とする電極再生方法。

【００３５】（２１）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素質電極が、有機質バインダーを使用して積層・圧縮した複数の繊維性シートを熱処理し、炭化及びグラファイト化したもので、この成型体を切削加工して、処理水の流通方向と前記繊維性シートの積層面とのなす角が１０～８０°となるように加工したことを特徴とする炭素質電極。

【００３６】（２２）　被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、前記２１記載の炭素質電極を使用することを特徴とする炭素質固定床型三次元電極電解槽。

【００３７】以下本発明を詳細に説明する。本発明の固定床型三次元電極電解槽は一対の給電用板状電極好ましくはメッシュ状の電極間に１以上好ましくは３～１５の多孔質の固定床を配置し、前記の一対の給電用電極に直流電圧を印加することによって、多孔質固定床を分極させ、この固定床に処理水を通して細菌、ウィルス、原虫などの微生物の除去・殺菌する水処理装置である。或いは被処理水中の金属成分の回収や不純物の電気化学的分解除去にも利用できるものである。

【００３８】本発明は、固定床型三次元電極電解槽を用いる被処理水中の微生物を電気化学的に処理する方法において、用いる炭素質固定床を１００～１３０℃の水蒸気雰囲気下で処理することで炭素質表面を活性化することによって、被処理水中の微生物を効率的に除去・殺菌するものである。即ち、本発明の炭素質固定床型三次元電極電解槽で被処理水中の微生物を除去する場合、一旦炭素質固定床に微生物が吸着し、これが電極上で電解処理されて殺菌されていると考えられており、本発明の処理によって微生物の電極上への吸着がしやすくなるため除去・殺菌効率が向上したと推定される。この炭素質固定床の処理は多孔質炭素電極板のみを処理してもよいが、多孔質炭素電極板、金属補助電極及びガスケットからなる炭素質固定床として処理してもよい。或いは電解槽内に配置された状態で電解槽容器ごと処理することも可能である。この場合、予め電解槽容器に通水して多孔質炭素電極板を水で濡らしておくと効果的である。この処理は、市販の滅菌用オートクレーブが利用できる。その場合、１２０℃，２ａｔｍ、２０分の処理が好ましい。この処理は新品の多孔質炭素電極板でも効果があるが、特に使用済みで微生物の吸着力が低下した多孔質炭素電極板に著しい効果を発揮する。使用済みの多孔質炭素電極板を再生する場合はアルカリ洗浄及び／又は酸洗浄（例えば０．０５～５Ｎ　ＮａＯＨ、０．０５～５Ｎ　ＨＣｌを通水、浸漬して有機物、無機物を除去する）と組み合わせて行うとより効果的である。

【００３９】本発明の別の態様は、被処理水を電気化学的に処理する際に、炭素質固定床型三次元電極電解槽に印加する電解電圧の極性を反転させる処理方法において、電解槽に印加する第１の電解電圧の極性が反転する際に、第１の電解電圧よりも低くかつ極性が逆の第２の電圧を印加することを特徴とする処理方法である。即ち、これは電解電圧の極性を反復反転させると殺菌効率が向上するという事実に基づいている。そのメカニズムは明らかではないが、前述のように炭素質固定床型三次元電極電解槽で被処理水中の微生物を除去・殺菌する場合、一旦炭素電極上に微生物を吸着させて、電解殺菌している。殺菌された菌は自然に剥離するものもあるが、電解電圧の極性を反復反転させることによって一旦吸着した菌が剥離しやすくなると推察される。これによって、新たな微生物が炭素質電極上に吸着しやすくなっていると考えられる。電解電圧の印加は通常定期的に極性を反転させている。これは被処理水中に含まれているＣａ，Ｍｇ，Ｓｉなどの成分が電解によって析出するため、これを再度溶解させて電極や電解槽が閉塞することを防いでいる。通常１５～６０分間隔で極性を反転させている。本発明では、電解処理のための第１の印加電圧の極性反転に加えて、電極再生のための第２の印加電圧の反復反転を行う。具体的には、第１の印加電圧を＋Ｅ１又は－Ｅ１とし、電極再生のための第２の印加電圧を＋Ｅ２又は－Ｅ２とすると、従来は１５～６０分間隔で＋Ｅ１→－Ｅ１→＋Ｅ１もしくは－Ｅ１→＋Ｅ１→－Ｅ１と反転させていたが、本発明ではこれに電極再生のための第２の印加電圧の反復反転工程を加える。第２の印加電圧の反復反転工程は第１の印加電圧の電圧印加過程のどこに挿入してもよいが、第１の印加電圧の極性が反転する際に挿入することが望ましい。即ち、＋Ｅ１→（－Ｅ２→＋Ｅ２）ｎ→－Ｅ１→（＋Ｅ２→－Ｅ２）ｍ→＋Ｅ１もしくは＋Ｅ１→－Ｅ１→（＋Ｅ２→－Ｅ２）ｌ→＋Ｅ１である。

【００４０】ここで、好ましくは＋Ｅ１と－Ｅ１は略等

しい時間印加し、印加時間は１回１５～６０ｍｉｎである。又、ｎ又はｍ又はｌは１以上の整数で特に使用している電解槽の固定床の数以上であることが望ましい。＋Ｅ２と－Ｅ２は略等しい時間印加し、印加時間は１回５～６０秒であることが望ましい。又、印加電圧Ｅ１と印加電圧Ｅ２は同じ電圧でも良いが、印加電圧Ｅ２は印加電圧Ｅ１より低い又は高い電圧でもよい。これによって、長期間にわたって、高い殺菌効率が得られるようになった。

【００４１】本発明の別の態様は被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、処理水にアルカリ金属のハロゲン化物を添加して処理する方法である。この方法は特に被処理水中に多量の有機物を含む場合に効果的である。例えば、食用鶏肉の加工工場では内臓を取り出した鶏肉を最終的に包装する前に冷水の入った処理槽内で洗浄している。このような洗浄水には多量の肉片、血液成分が含まれているため細菌が繁殖しやすい環境となっている。このように被処理水中に多量の有機物を含む場合、処理水にアルカリ金属のハロゲン化物を添加して処理することによって極めて効率的に殺菌が行えることが判明した。具体的には、被処理水に０．００５～０．５％となるようにＮａＣｌ、或いはＫＣｌなどを添加して処理する。この場合、次亜塩素酸などの持続性のある殺菌成分が生成されるため、前述の殺菌メカニズムとの相乗効果でより高い殺菌効率が得られる。特にこの方法は貯水タンク或いは処理水槽などの水を本装置で処理した後、貯水タンク或いは処理水槽に戻すといった循環処理を行う際に著しい効果が得られる。この時に使用される多孔質炭素質電極には孔径が０．３～３ｍｍの複数の貫通孔を設けることによって、連続運転時の流量の低下が抑制され、処理効率が向上することが明らかとなった。貫通孔の数は任意に設けることが可能であるが、複数の貫通孔の開孔面積の総和が炭素質電極の通水断面積の１～１０％であることが望ましい。

【００４２】ところで、炭素質固定床型三次元電極電解槽では炭素質電極の陽極酸化による崩壊が問題となっている。これを防止するために金属製などの補助電極によって炭素質電極をサンドイッチし、水の電解による酸素の発生を主にこの金属電極上で行わせることによって炭素電極の崩壊を防止している。しかしながら、金属製の補助電極と炭素電極が離れてしまうと著しい炭素電極の崩壊が発生するという問題があった。通常金属製の補助電極はメッシュ状のものが利用されており、厚みが１ｍｍ程度のものが用いられている。そのため外力によって歪みやすく、一度歪んでしまうと完全に平面に戻すのは困難であり、無理に戻そうとするとかえって凸凹に歪んでしまう。

【００４３】図２により説明すると、本発明の炭素質固定床型三次元電極電解槽〔図２（ｇ）〕は、図２（ａ）で示すように、多孔性炭素電極（炭素質固定床）１を、金属補助電極２、２′でサンドイッチし、全体をガスケット３で包んでいる炭素質固定床型三次元電極を複数個重ね合わせたものから構成される。炭素質固定床型三次元電極の斜視図を図２（ｂ）に示す。正常の場合は、図２（ｃ）に示すように、金属補助電極は平面であり、炭素質固定床と全体で接触している。しかし、上述したように、金属補助電極が歪んだ場合、歪んだ電極を用いると部分的に炭素電極と接触しない部分が生じ、その部分で電極崩壊が進行するという問題があった。

【００４４】そこで本発明の別の態様では、これを防止するための組み立て方法を提供する。即ち、被処理水を炭素質固定床型三次元電極を通過させて、電気化学的に処理する炭素質固定床型三次元電極電解槽において、炭素質固定床に接触している金属製補助電極が湾曲している場合、図２（ｆ）に示したように接する炭素電極に対しその略中央で接触するように金属製補助電極を配置する炭素質固定床型三次元電極電解槽の組み立て方法である。この場合、周辺部を弾性体からなるガスケットによって押さえつけることが望ましい。こうすることによって、電解槽に組み込んだときに周辺部はガスケットによって押さえつけられて金属製補助電極と炭素電極はほぼ密着し、更に周辺部はガスケットによって覆われているため、分極が抑えられており陽極酸化の影響も少ない。

【００４５】もう１つは、図２（ｄ）或いは（ｅ）に示したように、炭素電極に対しその周辺部で金属補助電極と接触するように金属製補助電極を配置する炭素質固定床型三次元電極電解槽の組み立て方法である。この場合、電解槽内の隣接する金属補助電極間の略中央にガスケットと一体となった或いは分離したスペーサーを設ける。このようにすることによってガスケット及び／又はスペーサーを介して各炭素電極及び金属補助電極間に通水方向に力が加わったとき、それぞれがきちんと接触して陽極酸化による炭素電極の崩壊を防止することができ、電極の消耗を減らすことができた。

【００４６】又、長期間の電解槽の運転によって、最も上流側に配置された炭素電極の上流面が下流側の他の炭素電極よりも崩壊し易いことが判明した。そのため、この問題を解決するため鋭意検討を行った結果、電解槽の最も上流側の固定床の上流側に微細孔を有する板を設けることによって解決することを見出した。具体的には、図１０（ｂ）に示すように、給電用電極の外側或いは給電用電極と隣接する炭素電極との間に通水性で多孔質の板を配置した。多孔質の板はガラス、セラミック、樹脂、繊維、不織布などが好ましく、厚みは０．５～５ｍｍで平均孔径５０～２００μｍのものが好ましく用いられる。これによって最も上流側に配置された炭素電極が他よりも崩壊し易いという問題は解決した。

【００４７】又、本発明の別の態様では、多孔性炭素質電極内にある炭素微粉などの異物を除く方法を提供す

る。即ち、被処理水を炭素質固定床型三次元電極を通過させて電気化学的に処理する炭素質固定床型三次元電極電解槽に用いられる炭素電極において、あらかじめ濡らした電極板に空気を送り込むことによって、内部の異物や炭素微粉を効率的に取り除くことができることが判明した。具体的には、図３（ａ）に示したように炭素質固定床型三次元電極１７又は多孔性炭素電極（炭素質固定床）１の外径より大きい内径を有する筒１４に、炭素質電極の側面部と筒との隙間の部分の流体のリークを防止するようにして、かつ炭素電極を水又は水性溶媒で濡らし、これを一方が弾性体の蓋１５で略閉じられた前記の筒に略水平状態で挿入することによって、炭素質固定床内の異物を外部へ取り出す方法である。図３（ａ）のように、上部にセットした多孔性炭素電極１は、ピストン１６により、下方に押され、図３（ｂ）まで降ろされる。多孔性炭素電極１内部にある炭素微粉などの異物は、下方の圧縮された空気の圧力により、矢印のように上方に吹き出される。ピストン１６の代わりに手で押してもよく、又弾性体の蓋１５の代わりに別の炭素質固定床型三次元電極１７を筒内に設置し、略密封空間を形成してもよい。

【００４８】或いは、炭素質固定床型三次元電極１７又は多孔性炭素電極（炭素質固定床）１が気密容器の一部の壁面を構成するように配置し、該炭素電極側面部又は端部と気密容器との隙間からの流体のリークが略無視できるようにガスケットなどを利用して配置する。この場合、図４（ａ）で示すように、下方の空気導入口１９から圧縮空気が送られて来るので、多孔性炭素電極１がずれないように、気密容器に支持体１８を設置しておく。多孔性炭素電極１の上部（気密空間の外側）の面に水又は水性溶媒を入れ電極を濡らすか、予め電極を濡らしておく。その後、気密容器内に空気又は不活性ガスを送り込んで加圧することによって、炭素電極内の異物が外部へ取り出される。もし、上部に水又は水性溶媒が貯えられていると、異物はこの水又は水性溶媒の中に出てくるので、この水又は水性溶媒を異物と一緒に廃棄する。この処理は図４（ａ）のように、１枚ずつでもいいが、図４（ｃ）に示すように、多数枚でもよい。図４（ｃ）において、炭素質固定床型三次元電極１７がそれぞれ接触せず、かつ、給水排水がスムースに行えるように、リング状のスペーサー９を使用する。

【００４９】また原理、構成は略同一であるが、図４（ｂ）に示すように、水又は洗浄液を霧吹きの要領で、気密容器内に空気を送り込んで加圧すると同時に気密容器内側に水や洗浄液を噴霧したり、逆に気密容器外側を水或いは洗浄液に浸しておくと効果的である。

【００５０】ところで、炭素質固定床型三次元電極電解槽に被処理水を水圧２ｋｇ／ｃｍ^{2}以上で送水すると炭素質固定床が水圧で下流側に動いてしまうため給電用電極と炭素質固定床との間隔或いは炭素質電極と金属補助

電極が離れてしまうため陽極酸化による炭素電極の崩壊が起きるという問題があった。そこで、本発明の別の態様では、処理槽内の被処理水を炭素質固定床型三次元電極電解槽を通過させて電気化学的に処理する炭素質固定床型三次元電極電解槽において、少なくとも上流側の給電用電極が弾性体で隣接する炭素質固定床に押さえつけられていることを特徴とする電解槽によってこの問題を解決することができた。具体的には、図５（ｂ）又は（ｅ）に示すようにバネを金属製バネ２１又は金属製の板バネ２１′として給電用電極への配線の一部として利用することもできる。板バネ２１′を用いる場合、板バネの形状は、電解槽の直径が小さい場合は、図１１（ａ）に示すように片側のみの板バネでもよいが、電解槽の直径が大きくなると、バネ圧も高く、また羽の数も図１１（ｂ）、図１１（ｃ）のように、多くする。板バネの形状は任意でよく、羽の数も任意である。又、板バネは金属製であるが、チタンが好ましく、白金メッキされたチタンが最も好ましい。

【００５１】図１２（ａ）に、金属製の板バネ２１′を用い、図１２（ｂ）に圧縮コイルバネ４１を用いた炭素質固定床型三次元電極電解槽の構成を示す。図１３に、図１２（ｂ）の下部の分解図を示すが、電極４′の中心に熔接された金属棒３９に圧縮コイルバネ４１がはめられ、金属製の導電棒４０により支えられている。外部からの電力は、導電棒４０と金属棒３９により電極４′に与えられるので、圧縮コイルバネ４１は導電性のあるものでも、ないものでもよい。

【００５２】更に、図５（ａ）のように、樹脂などの非導電性の素材を使用したバネ２０を用いて、別途給電用電極への配線をワイヤーとすることも可能である。或いは図５（ｃ）に示すように、球状、柱状のゴムなどの弾性体２２を利用することもできる。

【００５３】又、本発明の電解槽は長期間連続で運転を続けると次第に制菌性能が低下するという問題があった。そこでこの問題を解決するために鋭意検討を続けた結果、定期的に電解槽を加熱処理することによって制菌性能が再生することが明らかとなった。その理由は明らかにされていないが、連続運転で低下した炭素電極への菌の吸着力が再生するためではないかと推測される。本発明の電解槽は例えばポリカーボネート樹脂或いはテフロン樹脂などの耐熱性素材からなる容器からなる。使用するガスケット、スペーサーもＥＰＤＭ（エチレンプロピレンゴム）などの耐熱性の高い素材が好ましい。例えば、図６に示すように、電解槽の中には、加熱手段としてヒーター２４が設置されている。このヒーター２４は導線２５により外部から通電して、加熱する。又、電解槽は外側が断熱材２３で覆われていることが望ましい。加熱温度は７０℃以上であり、７０℃以上で数分～１時間、好ましくは１０～３０分間処理すると効果的である。

【００５４】これらの加熱手段は電解槽の上流側に設けられていることが望ましく、加熱処理中は電解槽内の処理水の流量はゼロないし、通水断面積１ｃｍ²あたり０．０５リットル／分以下であることが望まれる。加熱処理中は電解は停止することができる。加熱処理中或いは処理終了後に電解槽から排出される加熱された水は排出系に排出されるように流路が切り替えられるようになっていることが望ましい。

【００５５】更に、図７（ａ）に示したように熱源を循環系に設置して、電解槽の処理だけでなくフィルター・配管全てを加熱処理することが好ましい。図７（ａ）において、計測系は破線で、制御系は点線で示し、自動制御循環システムを示している。処理する水は水供給口２７から導入され循環水槽２８に溜められるが、液面センサー２９から信号が制御装置に入り、所定の量になるとバルブ３１を閉じ、水の供給を止める。循環水槽２８に入った水は、３方コック３０、ポンプ３５、圧力計３３、１０μｍのフィルター３４をへて、電解槽本体２６に導入され、水処理された後、流量計３２をへて、採水される。制菌性能が低下し、循環を幾度も繰り返すようになると、ヒーター２４をＯＮにし、循環水槽２８から３方コック３０、ポンプ３５、圧力計３３、１０μｍのフィルター３４をへて、電解槽本体２６に導入されるが、水量は上述したように、通水断面積１ｃｍ²あたり０．０５リットル／分以下にし、水が７０℃以上に加熱されるようにする。電解槽を通過した水は、３方コック３０を操作し排水部へ導かれ外部に排出される。あるいは、系全体を加熱処理することもでき、処理水がバルブ３１を通るように３方コック３０を動かし、採水と排水の間の経路を水が循環するようにして、加熱処理された水を系内で循環させる。加熱処理終了後、流量を０．０５リットル／分以上（好ましくは通常運転時の５０～１００％の流量）に増やし、一定時間（例えば１～３０分間）は排出系に排水した後、流路を切り替えて通常運転に復帰することができる。これらの操作は制御装置によって自動的にバルブの切り替え、ポンプの駆動、ヒーターのＯＮ／ＯＦＦなどを制御することができる。

【００５６】また、図７（ｂ）のようにラインの補助水槽３６にヒーターを設置し、ここで加熱された処理水を電解槽に送水して処理することもできる。更に、補助水槽３６に洗浄のための酸、アルカリなどを添加し、これを系内に循環供給することもでき、熱処理と別に又は同時に行うこともできる。なお、図７（ｂ）において、図７（ａ）で示した自動制御装置及び制御系、計測系のラインの図示は同一であるので省略した。

【００５７】本発明の電解槽は運転中の任意のタイミングで手動或いは自動で加熱処理することができる。好ましくは予め設定された間隔で、例えば１日～１ヶ月間隔で自動的に加熱処理されることが望ましい。

【００５８】本発明の炭素質固定床型複極式電解槽は、

複数個の炭素質固定床を収容する筒状体の下方の開口部の一部に支持体を設置することにより前記筒状体からの前記複数の炭素質固定床の離脱を容易に防止するようにした炭素質固定床型複極式電解槽である。本発明に係わる該炭素質固定床型複極式電解槽は被処理水の改質処理や水溶液中の銀イオンなどの金属イオン回収等に使用することができる。

【００５９】写真処理液、飲料水、プール水、熱交換器用冷却水、浴場水及び養魚用水等の被処理水を本発明に係わる電解槽で処理することにより被処理水殺菌等の改質が行われ、又被処理水が低濃度銀イオン含有溶液である該溶液から銀イオンが金属銀として回収される。

【００６０】又、本発明の電解槽により、被処理水中、細菌（バクテリア）、糸状菌（黴）、酵母、変形菌、単細胞の藻類、原生動物、ウィルス等の微生物の殺菌が行われその水質が改善される。

【００６１】即ち、被処理水を炭素質固定床型三次元電極電解槽に供給すると、該被処理水中の微生物は液流動によって前記電解槽の炭素質固定床や給電用電極ターミナル等に接触・吸着しそれらの表面で強力な酸化還元反応を受けたり高電位の電極に接触し、その活動が弱まったり自身が死滅して殺菌が行われると考えられる。

【００６２】本電解槽を被処理水の改質処理に使用する場合には、印加電位を陽極電位が実質的な酸素発生を伴わない＋０．２～＋１．２Ｖ（ｖｓ．ＳＣＥ）、陰極電位が実質的に水素発生を伴わない０～－１．０Ｖ（ｖｓ．ＳＣＥ）となるようにすることが望ましいが、液中物質が酸化還元反応を受けず液性の変化が生じない場合や又その反応量がさほど問題にならない場合にはより高い陽極電位を印加することができる。例えば厚さ９ｍｍの多孔性炭素質電極の両側に白金メッキした厚さ１ｍｍのチタン製メッシュ電極を設けこれらを８段重ねて各々隣接するチタン製メッシュ電極間隔を１ｍｍとし、８枚重ねた両端のチタン製メッシュ電極と給電用電極の間隔を１ｍｍとした電解槽の場合、２０～５０Ｖの電圧を該給電用電極に印加することができる。同じ条件で１１段重ねとした場合は３０～７０Ｖの電圧を該給電用電極に印加することができる。又本電解槽を銀や金などの金属回収用として使用する場合には電極上で金属イオンの還元が生ずるに十分な電位を印加すればよい。

【００６３】被処理水の改質の場合、特にプール水や製紙洗浄水のような大量処理の場合にガス発生が伴うと、発生するガスつまり酸素ガスと水素ガスは通常爆発限界内の混合比で発生し、爆発の危険を回避するために空気等の不活性ガスで希釈することが望ましく、例えば電解槽出口に発生する電解ガスの分離手段と分離後の該電解ガスを空気で希釈して電解ガス濃度が４容量％以下になるよう希釈する手段を設置することができる。

【００６４】プール水等の被処理水の場合、処理すべき水量は莫大で例えば１時間当たり数トンとなるため、処

理能力の大きい本発明の炭素質固定床型複極式電解槽の使用が望ましく、該電解槽の使用により処理すべき被処理水との接触面積を増大させることができ、これにより装置サイズを小さくし、かつ電気化学的処理の効率を上げることができる点で有利である。

【００６５】本発明の固定床型三次元電極電解槽における電極は、好ましくは一般に炭素質固定床型三次元電極と給電用電極を含み、該質固定床型三次元電極は前述の使用する電解槽に応じた形状を有し、前記被処理水が透過可能な多孔質材料、例えば粒状、球状、フェルト状、織布状、多孔質ブロック状等の形状を有する活性炭、グラファイト、炭素繊維等の炭素系材料から選択することができる。

【００６６】本発明の炭素質固定床は、平均孔径２０～１００μｍのポーラスカーボングラファイトが好ましい。これらは例えば、有機物バインダーを使用して積層した複数の植物繊維製シート例えば和紙などを不活性ガス雰囲気中で１０００℃以上の温度で熱処理して炭化させ更に加熱処理してグラファイト化した多孔質炭素電極板である。より好ましくは、複数の合成繊維製シートを有機物バインダーを使用して積層・プレスし、これを熱処理して炭化させ更に加熱処理してグラファイト化した多孔質炭素電極板が不純物も少なく気孔径の制御も容易なため好ましい。特に目的の気孔径に対して気孔径分布の幅がせまくシャープになるため、目詰まりが起こりにくくなる。このような用途に用いられる有機物バインダーにはフェノール樹脂やエポキシ樹脂などが利用できるが特にこれらに限定されるものではない。合成繊維製シートは布状に織ったものでもよいが、不織布でもよい。布或いは紙などを積層・プレス後、焼成して作成した炭素電極は、繊維の長軸が横方向に伸びているため、繊維の伸びている方向には水が流れ易い。電極板を作成する際に、繊維の長軸方向と未処理水の流通方向を一致させるように加工することによって、通水し易い電極板が得られるが、これだと積層した層間で剥離し易く、曲げ強度が低下するという問題が生じる。そのため電極板内の未処理水の流通方向に対し、プレスした面とのなす角度が斜め（１０～８０°好ましくは３０～６０℃）になるように加工することによって繊維の方向も斜めになる。このような電極板を用いることによって通水抵抗が少なく、目詰まりしにくい、曲げ強度の低下も少ない電極板を得ることができる。

【００６７】即ち、従来の炭素電極は、図８（ａ）に示すように、繊維の長軸が横方向（積層面上）に伸びているため、繊維の伸びている方向には水が流れ易い。電極板を作成する際に、図８（ｂ）に示すように、繊維の長軸方向と未処理水の流通方向を一致させるように加工することによって、通水し易い電極板が得られるが、積層した層間で剥離し易いため、曲げ強度が低下するという問題が生じる。そのためこの問題を解決するために鋭意

検討を重ねた結果、図８（ｃ）に示すように、電極板内の未処理水の流通方向と繊維の積層面とのなす角度αが斜め（１０～８０°好ましくは３０～６０℃）になるように加工することによって繊維の方向も斜めになる。このような電極板を用いることによって通水抵抗が少なく、目詰まりしにくい、曲げ強度の低下も少ない電極板を得ることができた。

【００６８】これらの炭素電極板は１つのガスケットの中に複数枚配置することも可能である。例えば厚さ９ｍｍ孔径５０μｍのポーラスグラファイト１枚でもいいし、厚さ３ｍｍ孔径５０μｍのものを３枚重ねて用いてもよい。更に、孔径や厚さは任意に変更することもでき、例えば中央に孔径１００μｍ、その両側に孔径５０μｍのポーラスグラファイトをサンドイッチして設置し、この３枚重ねたものを１つの固定床とすることもできる。

【００６９】これら複数の積層された炭素質固定床は上下両端が開口する筒状体に収容する。該筒状体は、長期間の使用又は再度の使用にも耐え得る電気絶縁材料で形成することが好ましく、特に合成樹脂であるポリエピクロルヒドリン、ポリビニルメタクリレート、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化エチレン、フェノールーホルムアルデヒド樹脂、ＡＢＳ樹脂、アクリル樹脂、ポリカーボネート等が使用できる。更に透明又は半透明な材料で成形すると、前記炭素質固定床の消耗状態を視認できるためより好都合である。

【００７０】この筒状体に収容された前記複数の炭素質固定床はその直径が前記筒状体の内径よりも同等かやや小径であるため、該筒状体のみを把持して前記炭素質固定床の交換等の操作を行うと該炭素質固定床が下方の開口部から離脱して所定数の炭素質固定床を筒状体内に収容できなくなる。

【００７１】従って本発明に係わる電解槽では、前記筒状体の下方或いは上部の開口部の一部を閉塞するように支持体を設置して前記炭素質固定床の離脱つまり筒状体からの落下等を防止することが好ましい。該支持体の形状は前記複数の炭素質固定床の移動を抑制するだけの強度を有すれば特に限定されず、前記筒状体の下端部にドーナツ状体を該ドーナツ状体が開口部の一部を塞ぐように溶接や接着等により固定したり、或いはこれと同一形状の部材を一体成型したり、十字型の部材を筒状体の下端の円周部分に跨がるよう接着等により固定したり、或いは網状体を同様に前記開口部内に設置したりすることができる。又前記ドナーツ状体及び筒状体にネジを刻設して両部材をネジ止めして相互に固定することもできる。又開口部の上部も同様にネジ止めにより支持体を設置することができ、これらより前記炭素質固定床をより安定な状態で前記筒状体内に収容することができる。

【００７２】なお該支持体の被処理水の流れ方向に垂直方向の断面積は、開口部の開口面積の３～５０％とする

ことが望ましく、３％未満であると強度不足による該支持体の筒状体からの離脱が生じ易くなり、又５０％を越えると被処理水の流通を阻害するとともに電解電圧の上昇を招き易くなる。

【００７３】該炭素質固定床を直流又は交流電場内に置き、両端に設置した平板状又はエキスパンドメッシュ状やパーフェレーティッドプレート状等の多孔板体から成る給電用電極ターミナル間に直流電圧或いは交流電圧を印加して前記炭素質固定床を分極させ該炭素質固定床の一端及び他端にそれぞれ陽極及び陰極を分極により形成させて成る三次元電極を収容した炭素質固定床型複極式電解槽とすることが可能であり、この他に単独で陽極として或いは陰極として機能する三次元材料を交互に短絡しないように設置しかつ電気的に接続して炭素質固定床型複極式電解槽とすることができる。

【００７４】前記給電用陽極ターミナルの材質としては、例えばカーボングラファイト材（炭素繊維、カーボンクロス、グラファイト等）、グラシーカーボン、炭素複合材（炭素に金属を粉状で混ぜ焼結したもの等）、活性炭素繊維不織布（例えばＫＥ－１０００フェルト、東洋紡株式会社）又はこれに白金、パラジウムやニッケル等を担持させた材料、更に寸法安定性電極（白金族酸化物被覆チタン材）、白金被覆チタン材、ニッケル材、ステンレス材、鉄材等から形成される材質がある。又該給電用陽極ターミナルに対向し負の直流電圧を与える給電用陰極ターミナルは、例えば白金、ステンレス、チタン、ニッケル、銅、ハステロイ、グラファイト、炭素材、軟銅或いは白金族金属を被覆した金属材料等から形成されることができる。

【００７５】前記炭素質固定床として活性炭、グラファイト、炭素繊維等の炭素系材料を使用しかつ陽極から酸素ガスを発生させながら被処理水を処理する場合には、前記炭素質固定床が酸素ガスにより酸化され炭酸ガスとして溶解し易くなる。これを防止するためには前記炭素質固定床の陽分極する側にチタン等の基材上に酸化イリジウム、酸化ルテニウム等の白金族金属酸化物を被覆し補助電極として使用される多孔質材料又は網状材料を接触状態で設置し、酸素発生が主として該材料上で生ずるようにすることが望まれる。前記金属を用いた補助電極のかわりに、表面開孔率が１０～８０％となるようにΦ０．１～３mmの複数の通水用細孔を有するグラッシーカーボンなどの炭素材（厚さ０．５～２．０mm）を前記ポーラスカーボングラファイトなどの炭素電極に電気的に密着させて使用することもできる。

【００７６】処理すべき被処理水が流れる電解槽内に液が炭素質電極材料に接触せずに流通できる空隙があると被処理水の処理効率が低下するため、炭素質固定床等は電解槽内の被処理水の流れがショートパスしないように配置することが重要である。そのため、炭素質電極材料の周辺部及び側面部を一つのガスケットで覆うことによって、このリーク流を防止することができる。このような電解槽を組み立てる場合の例を示す。即ち、予めガスケットに炭素質電極材料及び金属補助電極を組み込んだ固定床を作製する。ガスケットはゴム等の弾力性のある素材からできているため、炭素質電極材料或いは金属補助電極の実際の寸法よりもやや小さめに作製しておき、引き伸ばしながらはめ込んでやると密着性の点で好ましい。また、炭素質電極材料の側面部のガスケットが通水時の水圧によって広がり、ここからリークすることを防止するため、固定床を収容する容器内径よりやや大きい外径の突起を設けることが好ましい。又、金属補助電極は炭素質電極材料とともにはさみこんでもよいし、炭素質電極材料の上にそえてもよい。

【００７７】前述のリーク防止のために電極と電解槽容器との隙間に樹脂を充填する方法もある。このような樹脂に熱硬化性樹脂やシリコンシーラントなどが用いられる。或いは電極板を熱収縮チューブに詰めて加熱処理してもよい。ただし、一度樹脂で固めてしまうと分解が容易ではなくなるという欠点がある。

【００７８】補助電極と炭素電極を導電性樹脂で接着することも可能であり、陽極酸化による炭素電極の崩壊を抑制するために有効である。

【００７９】又、これらの電解槽は被処理水中の異物や陽極酸化によって生じる炭素微粉末のために目詰まりを起こしやすいという問題があった、そのため、炭素質電極材料の被処理水流入側に複数の非貫通の孔をあけた炭素質電極材料を用いることによって、異物や炭素微粒子による目詰まりが著しく抑制されることが判明した。孔の深さは炭素質電極材料の１／４から３／４が好ましく、孔径は０．５～４．０mmが好ましい。孔の部分の面積は炭素質電極材料の５～２５％が好ましい。

【００８０】又前記電解槽に供給される被処理水の流量は、該被処理水が効率的に電極等の表面と接触できるように規定すればよく、完全な層流であると横方向の移動が少なく炭素質固定床表面との接触が少なくなるため、乱流状態を形成するようにすることが好ましく、５００以上のレイノルズ数を有する乱流とすることが特に好ましい。

【００８１】このような構成から成る電解槽は、例えば写真処理液中の微生物の殺菌用として使用する場合には、発色現像槽、漂白槽、漂白定着槽、水洗工程槽や安定化工程槽等の写真処理工程の一部又は全部の槽に接続して、前記各処理槽中の写真処理液を前記電解槽に供給し循環して処理を行う。又写真処理液からの銀回収用として使用する場合も同様に写真処理槽に近接させて設置し、銀イオンを含む定着液等を前記電解槽に供給しながら通電して銀を回収することができる。

【００８２】更に本発明の電解槽は、ビルやマンションの屋上等に設置された熱交換器、或いはプール、或いは製紙工程、更に養殖場や釣堀等、浄水場の貯留ライン或

いは家庭や飲食店の水道の蛇口、又は銭湯や温泉等の営業用浴場や家庭用の浴槽に設置して、それぞれの被処理水を前記電解槽に導入し電気化学的に処理することにより、前記被処理水の殺菌等の改質処理を行うことができる。

【００８３】なお、本発明の電解槽では該電解槽に漏洩電流が生じ該漏洩電流が電解槽から写真処理液等の被処理水を通して他の部材例えば写真処理槽に流れ込み、該写真処理槽中で好ましくない電気化学反応を誘起したり、写真処理槽の壁面を電気化学的に腐食させ壁面構成材料を溶出させることがあるため、電解槽内の陽陰極が相対しない電極背面部及び／又は前記電解槽の出入口配管内に、前記被処理液より導電性の高い部材をその一端を接地可能なように設置して前記漏洩電流を遮断することができる。これは、他の被処理水に対しても有効である。

【００８４】次に添付図面に基づいて本発明に係わる炭素質固定床型三次元電極電解槽の好ましい例を説明するが、本発明の電解槽は、この電解槽に限定されるものではない。

【００８５】各図において、例えばポーラスカーボングラファイト電極の炭素質固定床１が積層され、その炭素質固定床は、金属補助電極（例えば白金メッキされたチタンメッシュ）２及び２′でサンドウィッチされる。炭素質固定床と補助電極は弾性のあるガスケット（例えばゴム製）３により保持され、電解槽の内面に密着する。電解槽の入り口（ＩＮ）から被処理水が０．５～５ｋｇｆ／ｃｍ^{2}の圧力で送水され、電極４及び４′に外部より電圧をかけることにより、被処理水は、殺菌され、上部の（ＯＵＴ）から取り出される。

【００８６】図１は、比較の炭素質固定床型三次元電極電解槽の断面図である。上部の入り口（ＩＮ）から導入された被処理水は、電解槽の内筒５と外筒６の間のスペース７（被処理水導入路）を通り電極内を通過してＯＵＴに到達する。矢印に従って被処理水が通過する際に、外部から、電極ターミナル１１、１１′をへて電極４、４′から電力が供給され、金属補助電極２、２′に挟まれた炭素質固定床炭素電極１を通過する際に、被処理水中に含まれる細菌の殺菌或いは銀などの回収が行われる。炭素質固定床は金属補助電極２、２′に挟まれ積層されているので、下部から上部に亙り分極している。それぞれの、炭素質固定床１と金属電極２、２′は側部から被処理水がリークしないように、ガスケット３で封鎖＊

＊されている。これらの組がセットされるように、上蓋１０と外筒６はネジで組み立てられている。洗浄の際に、内部の水を排出する水ぬき栓１３と最初に被処理水がスムースに導入されるように、空気ぬき栓１２が設けられている。

【００８７】

【実施例】次に本発明を実施例に基づき説明するが、本発明の実施態様はこれに限定されない。

【００８８】実施例１

合成繊維を骨材とし、有機物バインダーで重ねあわせて２００ｋｇｆ／ｃｍ^{2}の圧力で成型し、この成型物を熱処理し、厚さ９ｍｍのポーラスカーボングラファイトを作成した。気孔率６０％、平均気孔径５１μｍであった。これを比較の多孔性炭素電極とした。更に、このポーラスカーボングラファイトを水で濡らし、オートクレーブにて１２０℃、２ａｔｍ，２０ｍｉｎ処理し、本発明の多孔性炭素電極を得た。

【００８９】本発明の多孔性炭素電極だけを用いて、図１に示した電解槽を作成した。又、同様に比較の多孔性炭素電極を用いて電解槽を作成した。

【００９０】固定床はポーラスカーボングラファイトで厚み９ｍｍ、直径７６ｍｍである。

【００９１】金属補助電極として白金で被覆されたチタンメッシュ（厚み１ｍｍ）を用いて、前記ポーラスカーボングラファイトをサンドイッチした。本電解槽には給電用電極端子に直流３４Ｖを印加し、３０分間隔で極性を反転させた。本電解槽の場合、電圧は２０～５０Ｖの範囲で任意に変更できる。

【００９２】制菌性能試験はＰｓｅｕｄｏｍｏｎａｓ ｄｉｍｉｎｕｔａを液体培地（普通ブイヨン培地、栄研化学製）を用いて１日間培養し、菌体を５０００ｒｐｍにて遠心分離した後、純水で洗浄し、再度遠心分離した。これを予めためておいた水道水（残留塩素濃度が０．０１ｐｐｍ以下）に添加し被処理水とした。これを本発明の多孔性炭素電極を用いた電解槽及び比較の多孔性炭素電極を用いた電解槽に１．２ｋｇ／ｃｍ^{2}の圧力で送水し、電解槽通過前後の被処理水を採水し、これに含まれる生菌数を普通寒天培地（栄研化学製）を用いた寒天平板法にて測定した。その結果を表１に示す。被処理水は、生菌数の異なる２種類、１及び２を用いた。制菌率は下記の式から算出した。

【００９３】

【数１】

$$\text{制菌率（％）} = \left(1 - \frac{\text{電解槽通過後の処理水中の生菌数（ＣＦＵ／ｍℓ）}}{\text{電解槽通過前の処理水中の生菌数（ＣＦＵ／ｍℓ）}}\right) \times 100$$

【００９４】

【表１】

23　　24

	被処理水	生菌数測定結果(CFU/m ℓ)		制菌効率%
		IN側	OUT側	
本発明の電解槽	1	8.6×10^{4}	8.3×10^{1}	99.9%
	2	3.1×10^{3}	1.2×10^{1}	99.6%
比較の電解槽	1	8.2×10^{4}	1.1×10^{4}	86.6%
	2	3.5×10^{3}	5.6×10^{2}	84%

【００９５】表１から、本発明の多孔性炭素電極を用いた電解槽の方が明らかに制菌効率に優れていることが判明した。

【００９６】実施例２

実施例１で使用した比較の電解槽と同じ電解槽を用意し＊た。これらの給電用電極に各々下記表２に示すパターンの電圧をくり返し印加した。

【００９７】

【表２】

	電　圧　印　加　方　法
比較の電圧印加方法	40v(15min)→－40v(15min)→40v(15min)
本発明の電圧印加方法－１	40v(15min)→－40v(15min)→(40v(15sec)→－40v(15sec))8→40v(15min)
本発明の電圧印加方法－２	40v(15min)→－40v(15min)→(25v(30sec)→－25v(30sec))8→40v(15min)

【００９８】各電圧印加方法について、下記の方法で制菌性能を比較した。実施例１と同様の方法でＰｓｅｕｄｏｍｏｎａｓ　ｄｉｍｉｎｕｔａ（約10^{5}ＣＦＵ／ｍｌ）を含む被処理水を各２０リットル調整し、水槽に用意した。図９に示した装置で、実施例１の比較の電解槽に該被処理水を２リットル／分の圧力で送水し、電解槽通過後の被処理水を再度水槽に戻してくり返し処理を行※った。処理開始時及び処理開始３時間後に水槽内の被処理水を採水し、これに含まれる生菌数を普通寒天培地（栄研化学製）を用いた寒天平板法にて測定した。その結果を表３に示す。

【００９９】

【表３】

	開始時の生菌数	３時間後の生菌数
比較の電圧印加方法	3×10^{5}CFU／ml	2×10^{3}CFU／ml
本発明の電圧印加方法－１	3×10^{5}CFU／ml	5×10^{1}CFU／ml
本発明の電圧印加方法－２	3×10^{5}CFU／ml	1×10^{2}CFU／ml

【０１００】表３から本発明の電圧印加方法が制菌性能に優れていることが確認された。

【０１０１】実施例３

実施例１で使用した比較の電解槽と同じ電解槽を用意し、これらを、図９に示した循環処理システムの電解槽としてそれぞれ設置した。

【０１０２】制菌性能試験はＥｓｃｈｅｒｉｃｈｉａ　ｃｏｌｉを液体培地（普通ブイヨン培地、栄研化学製）を用いて１６時間培養し、菌体を５０００ｒｐｍにて遠心分離した後、純水で洗浄し、再度遠心分離した。これを予めためておいた水道水（残留塩素濃度が０．０１ｐｐｍ以下）に添加し、更に異なる濃度のＮａＣｌを添加

して被処理水とした。

【０１０３】この被処理水２０リットルをそれぞれ図９に示した循環水槽２８に入れた。電解槽には３４Ｖを印加し１５分ごとに極性を反転させ、ポンプで１リットル／ｍｉｎの流量で３０分間循環処理を行った。処理前及び処理後の被処理水を採水し、含まれる生菌数をデソキ＊シコーレート寒天培地（栄研化学製）を用いて測定した。被処理水に何も加えない場合を比較例４１、ハロゲン化アルカリを加えた場合を本発明例４１～４３とし、結果を表４に示す。

【０１０４】

【表４】

		処理前の生菌数	循環処理後の生菌数
比較例41	0%　NaCl	2×10^5CFU／ml	5×10^1CFU／ml
本発明例41	0.01% NaCl	2×10^5CFU／ml	0 CFU／ml
本発明例42	0.1%　NaCl	2×10^5CFU／ml	0 CFU／ml
本発明例43	0.05% KCl	2×10^5CFU／ml	0 CFU／ml

【０１０５】表４から本発明の被処理水の処理方法が制菌性能に優れていることが確認された。

【０１０６】実施例４

実施例１のポーラスカーボングラファイト多孔性炭素電極にΦ１ｍｍ及び３ｍｍの貫通孔を設け、それぞれの貫通孔を有するポーラスカーボングラファイトからなる電解槽を２つ作成した。孔がない比較の多孔性炭素電極を用いて電解槽を作成し、図９に示したような循環処理システムを用意した。

【０１０７】実施例１と同様の方法でＰｓｅｕｄｏｍｏｎａｓ　ｄｉｍｉｎｕｔａ（約10^4ＣＦＵ／ｍｌ）を含む被処理水を調整し、これにＮａＣｌを０．０４％となるように添加し、これを水槽に３０リットル用意し※た。各々の電解槽ごとに該被処理水を３リットル／分の流量で送水し、電解槽通過後の被処理水を再度水槽に戻してくり返し処理を行った。処理開始時及び処理開始１週間後及び２週間後の流量（水圧１．２ｋｇ／ｃｍ^{2}で送水）と水槽内の被処理水の生菌数を普通寒天培地（栄研化学製）を用いた寒天平板法にて測定した。孔がない多孔性炭素電極を用いて電解槽を用いた比較例５１、５２とΦ１ｍｍ及び３ｍｍの貫通孔を有するポーラスカーボングラファイトからなる電解槽を用いた本発明例５１、５２の結果を表５に示す。

【０１０８】

【表５】

	ポーラスカーボングラファイトの貫通孔の数（１枚あたり）	被処理水に添加したNaCl濃度	生菌数 CFU／ml			流量 リットル／min		
			開始	7日後	14日後	開始	7日後	14日後
比較例51	なし	0%	10^4	10^2	10^2	3.9	3.5	3.2
比較例52	なし	0.04%	10^4	<10	<10	3.9	3.7	3.4
本発明例51	Φ1mm×150コ	0.04%	10^4	<10	<10	4.8	4.8	4.7
本発明例52	Φ3mm×50コ	0.04%	10^4	<10	<10	5.4	5.4	5.3

【０１０９】循環開始後、ポータブル残留塩素計（ハック社製）で全残留塩素を測定したところ、比較例５１では０．０４ｐｐｍであり、比較例５２では０．６ｐｐｍであった。本発明例５１で２ｐｐｍ、本発明の例５２で１．８ｐｐｍであり、運転開始後短時間で濃度の上昇が認められた。

【０１１０】本発明の貫通孔を有する電解槽でアルカリ金属のハロゲン化物を添加した被処理水を循環処理することによって、連続運転時の流量の低下が抑制され、処理効率が向上することが明らかとなった。

【０１１１】実施例５

図２（ｆ）又は（ｅ）に示した金属補助電極と炭素電極及びガスケット或いは更にスペーサーからなる炭素質固定床を組み立て、これを用いて図２（ｇ）に示した電解槽を作成し、本発明の電解槽（６１）、（６２）とした。又、図２（ｄ）に示したような歪んだ金属補助電極と炭素電極及びガスケット或いは更にスペーサーからなる炭素質固定床を組み立てこれを用いて図１に示した電解槽を作成し比較の電解槽（６１）とした。また参考例として図２（ｃ）に示したような実質的に歪みのない金属補助電極と炭素電極及びガスケット或いは更にスペーサーからなる炭素質固定床を組み立てこれを用いて図１に示した電解槽（６１）を作成し、これを参考例とした。これらの電解槽には、以下の炭素電極及び金属補助電極を用いた。

【０１１２】炭素電極：ポーラスカーボングラファイトΦ７６ｍｍ×厚み９ｍｍ、平均気孔径６０μｍ、気孔率６５％

27

金属補助電極：白金被覆チタンメッシュ厚み１ｍｍ
電解槽：炭素電極８枚、極間１ｍｍ
電解条件：ＤＣ５０Ｖ、３０ｍｉｎごとに極性反転
各々の電解槽を図９のように設置し、水槽に水道水（電気伝導度３００μＳ／ｃｍ）５０リットルを用意し、ポンプにて１．２ｋｇｆ／ｃｍ^{2}の水圧で送水し、９６時＊

28

＊間電解を行った。炭素電極の陽極酸化崩壊率は７２時間電解後の重量減少率をその指標とした。それぞれの結果は、対応する例として表６に示す。

【０１１３】

【表６】

	比較例61	参考例61	本発明例61	本発明例62
重量減少率	0.5%	0.2%	0.2%	0.2%

【０１１４】このように湾曲した補助電極を用いても、本発明の組み立て方法でつくった電解槽は炭素電極の陽極酸化による崩壊が少なく優れていることが確認された。

【０１１５】実施例６

図１０（ａ）に示した電解槽を比較例７１とし、これに図１０（ｂ）に示したように炭素電極の上流側に平均孔径５０μｍ厚さ３ｍｍの多孔質板３７を設け、これを本発明例７１の電解槽とした。これらの電解槽には、以下の炭素電極及び金属補助電極を用いた。

【０１１６】炭素電極：ポーラスカーボングラファイトΦ７６ｍｍ×厚み９ｍｍ、平均気孔径５０μｍ、気孔率※

※６１％

金属補助電極：白金被覆チタンメッシュ厚み１ｍｍ
電解槽：炭素電極８枚、極間１ｍｍ
電解条件：ＤＣ５０Ｖ、３０ｍｉｎごとに極性反転
各々の電解槽を図９のように循環系に設置し、水槽に水道水（電気伝導度３１０μＳ／ｃｍ）３０リットルを用意し、ポンプにて１．２ｋｇｆ／ｃｍ^{2}の水圧で送水し、９６時間電解を行った。炭素電極の陽極酸化崩壊率は７２時間電解後の最も上流側の炭素電極の重量減少率をその指標とした。その結果を表７に示す。

【０１１７】

【表７】

	比較例71	本発明例71
最も上流側の炭素電極の重量減少率	0.6%	0.2%
中段の炭素電極の重量減少率	0.2%	0.2%

【０１１８】このように本発明の電解槽では最も上流側の炭素電極の陽極酸化による崩壊が少なく優れていることが確認された。

【０１１９】実施例７

実施例１で使用した比較の電解槽と同様の電解槽を用意し、図９に示した循環系を組んだ。炭素電極には下記のものを使用した。

【０１２０】炭素電極：ポーラスカーボングラファイトΦ７６ｍｍ×厚み９ｍｍ、平均気孔径４２μｍ、気孔率６０％

電解槽には実施例２の比較の電圧印加方法で電圧を印加した。

【０１２１】水道水２０リットルを水槽に用意した。該被処理水を２リットル／分の流量で送水し、電解槽通過後の被処理水を再度水槽に戻してくり返し処理を行った。３週間循環処理した後、電解槽を分解した。分解後、流水で１５分間洗浄し、このとき炭素電極から出てきた炭素微粉などの異物を採取し、採取された異物の重量を測定し比較例８１とした。

【０１２２】この炭素電極を濡らした状態で図３に示した装置の円筒に押し込み、図３に示すように、ピストン１６を押して〔図３（ａ）→図３（ｂ）〕炭素電極内にエアを送り込むことによって内部の異物を取り出した。この操作を１０回繰り返し本発明例８１とした。

【０１２３】別の操作として、図４（ａ）に示した装置にセットし１０分間炭素電極内にエアを送り込むことによって内部の異物を取り出し本発明例８２とした。更に洗浄後の電極で再度電解槽を組み立て１．２ｋｇｆ／ｃｍ^{2}で送水したときの流量をそれぞれ測定した。表８にそれぞれの方法で採取された異物の炭素電極１枚あたりの重量と洗浄後の電極で再度電解槽を組み立て１．２ｋｇｆ／ｃｍ^{2}で送水したときの流量を示した。

【０１２４】

【表８】

	異物の重量（g）	流　量（リットル／min）
比較例81（流水洗浄）	0.011	1.7
本発明例81（図３の装置を使用）	0.018	2.0
本発明例82（図４（ａ）の装置を使用）	0.021	2.0

29

【０１２５】本発明例８１又は８２が電極内の異物の除去に有効であり、これによって電極の閉塞が改善され流量が改善されることが確認された。

【０１２６】実施例８

図５（ａ）及び図５（ｅ）に示した電解槽を用意した。即ち、上流側の給電用電極をバネで支持し、隣接する炭素電極に密着させたものである。これをそれぞれ本発明の電解槽とした。また、図５（ｄ）に示した電解槽を比較例とした。

【０１２７】これらの電解槽には、以下の炭素電極及金属補助電極を用いた。

【０１２８】炭素電極：ポーラスカーボングラファイトΦ７６ｍｍ×厚み９ｍｍ、平均気孔径５１μｍ、気孔率６０％

金属補助電極：白金被覆チタンメッシュ厚み１ｍｍ

電解槽：炭素電極８枚、極間１ｍｍ

電解条件：ＤＣ４５Ｖ、３０ｍｉｎごとに極性反転

各々の電解槽を図９のように設置し、循環水槽２８に水道水（電気伝導度３１０μＳ／ｃｍ）３０リットルを用意し、ポンプにて２．８ｋｇｆ／ｃｍ^{2}の水圧で送水し、１週間電解を行った。炭素電極の陽極酸化崩壊率は最も上流側の炭素電極の重量減少率をその指標とした。その結果を表９に示す。

【０１２９】

30

＊【表９】

	最も上流側の炭素電極の重量減少率
比較例91	0.7%
本発明例91	0.4%
本発明例92	0.4%

【０１３０】このように本発明の電解槽では最も上流側の炭素電極の陽極酸化による崩壊が少なく優れていることが確認された。

【０１３１】実施例９

本発明の電解槽として、図６に示した電解槽を組み立て、図７（ａ）に示した循環システムを組んだ。図１の電解槽を図９の循環システムに組み込んでこれを比較例とした。

【０１３２】実施例１と同様の方法でＰｓｅｕｄｏｍｏｎａｓ　ｄｉｍｉｎｕｔａ　（約１０５ＣＦＵ／ｍｌ）を含む被処理水を各５０リットル調整し、水槽に用意した。本発明の電解槽に該被処理水を１．２ｋｇｆ／ｃｍ^{2}の圧力で送水し、電解槽通過後の被処理水を再度水槽に戻してくり返し処理を行った。処理開始時及び処理開始３日ごとに、下記表１０に示す加熱処理を実施した。

【０１３３】

＊【表１０】

	通常運転	加熱工程	洗浄工程	通常運転
流量（リットル／min）	3	0～0.05	0.1→3	3
排出先	循環水槽	排水	排水	循環水槽
電解電圧	34V	0V	34V	34V
ヒーター	OFF	ON	OFF	OFF
電解槽温度	25℃	25→90℃（70℃以上で15min）	85→25℃	25℃
処理時間	3日間	25min	5min	3日間

【０１３４】運転開始１ヶ月後に本発明の電解槽の制菌性能試験を実施例１の方法で行った。

【０１３５】同様に、比較の電解槽に被処理水を１．２ｋｇｆ／ｃｍ^{2}の圧力で送水し、電解槽通過後の被処理水を再度水槽に戻してくり返し処理を行った。運転開始１ヶ月後に比較の電解槽の制菌性能試験を実施例１の方法で行った。

【０１３６】その結果を表１１に示す。

【０１３７】

【表１１】

	制菌率
比較例111	86%
本発明例111	99%

【０１３８】このように本発明の電解槽及び再生方法を施した電解槽は長期間にわたって高い制菌性能が維持されることが確認された。

【０１３９】実施例１０

図８（ｃ）のポーラスカーボングラファイト（角度α＝６０°）を用いて、図１の電解槽を組み立て本発明の電解槽とした。また、図８（ａ）のポーラスカーボングラファイトを用いて、図１の電解槽を組み立て比較の電解槽とした。

【０１４０】炭素電極には下記のものを使用した。

【０１４１】炭素電極：ポーラスカーボングラファイトΦ７６ｍｍ×厚み９ｍｍ、平均気孔径４２μｍ、気孔率６１％

金属補助電極：白金被覆チタンメッシュ厚み１ｍｍ

電解条件：ＤＣ４０Ｖ、３０ｍｉｎごとに極性反転

31

各々の電解槽を用いて、実施例１の方法で制菌性能を試験した。更に、図９に示した循環系を組み、１．２ｋｇ／ｃｍ²の水圧で送水して１ヶ月間連続運転を行い、そ＊

32

＊の間の流量を測定した。その結果を表１２に示す。

【０１４２】

【表１２】

	制菌率%	流量循環開始時	流量１ヶ月後
比較例121	93%	3.5リットル／min	2.4リットル／min
本発明例121	96%	3.9リットル／min	3.6リットル／min

【０１４３】本発明の炭素電極を用いた電解槽は制菌性能に優れ、流量低下も少なく優れていることが確認された。

【０１４４】

【発明の効果】本発明により、炭素質固定床型三次元電極電解槽を用いる被処理水中の微生物等を電気化学的に処理する方法において、制菌効率に優れ、流量低下が少ない電解槽及び処理方法を提供することができた。

【図面の簡単な説明】

【図１】炭素質固定床型三次元電極電解槽の断面図である。

【図２】本発明の炭素質固定床型三次元電極の組み立て方法の説明図である。

【図３】本発明の炭素質固定床型三次元電極から異物を取り除く方法を示す図である。

【図４】本発明の炭素質固定床型三次元電極から異物を取り除く別の方法を示す図である。

【図５】本発明の炭素質固定床型三次元電極電解槽の異なった構成を示す断面図である。

【図６】本発明の炭素質固定床型三次元電極電解槽にヒーターを組み込んだ１例を示す断面図である。

【図７】本発明の水処理方法における炭素質電極の再生システムを含む循環処理システムを示す図である。

【図８】炭素質電極の断面図である。

【図９】本発明の水処理方法における循環処理システムを示す図である。

【図１０】本発明の炭素質固定床型三次元電極電解槽の異なった構成を示す断面図である。

【図１１】本発明の炭素質固定床型三次元電極電解槽の上流側の給電用電極を支持する金属製の板バネの代表例の２面図である。

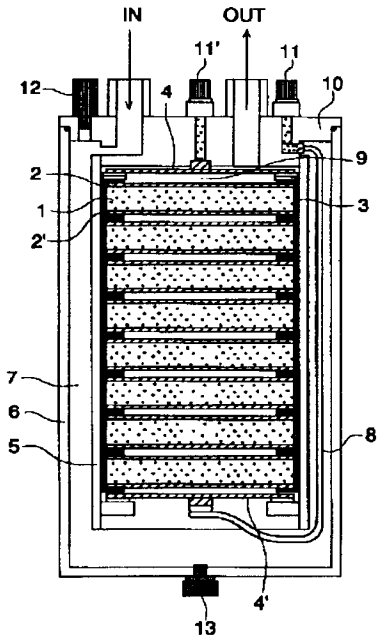
【図１２】本発明の炭素質固定床型三次元電極電解槽の上流側の給電用電極を支持する異なった構成を示す断面図である。

【図１３】本発明の炭素質固定床型三次元電極電解槽の上流側の給電用電極を支持する圧縮コイルバネを中心とした分解図である。

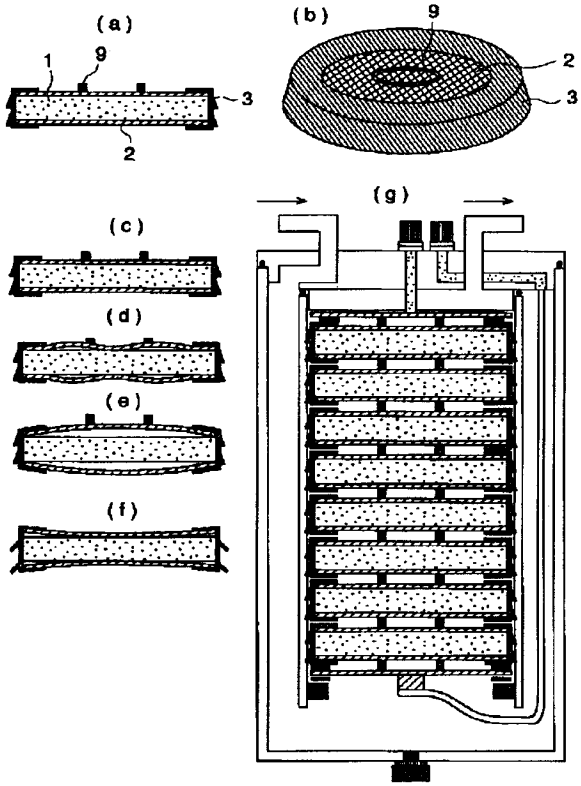
【符号の説明】

１　多孔性炭素電極（炭素質固定床）
２　金属補助電極
２′　金属補助電極
３　ガスケット
４　電極（外部から電力供給用）
４′　電極（外部から電力供給用）
５　内筒
６　外筒
７　被処理水導入路
８　導線
９　スペーサー
１０　上蓋
１１　電極ターミナル
１１′　電極ターミナル
１２　空気抜き栓
１３　水抜き栓
１４　筒
１５　弾性体の蓋
１６　ピストン
１７　炭素質固定床型三次元電極
１８　支持体
１９　空気導入口
２０　バネ
２１　金属製バネ
２１′　金属製の板バネ
２２　弾性体
２３　断熱材
２４　ヒーター
２５　ヒーター用の導線
２６　電解槽本体
２７　水供給口
２８　循環水槽
２９　液面センサー
３０　３方コック
３１　バルブ
３２　流量計
３３　圧力計
３４　フィルター
３５　ポンプ
３６　補助水槽
３７　多孔質板
３８　電解槽容器
３９　金属棒
４０　導電棒
４１　圧縮コイルバネ

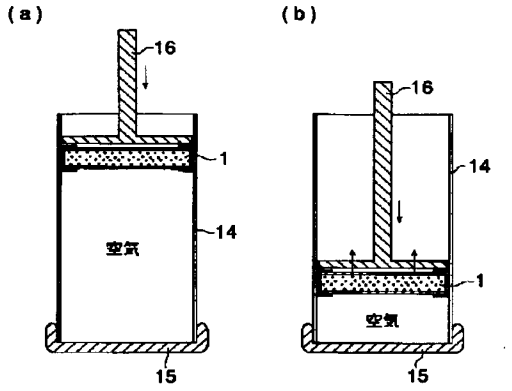
【図１】



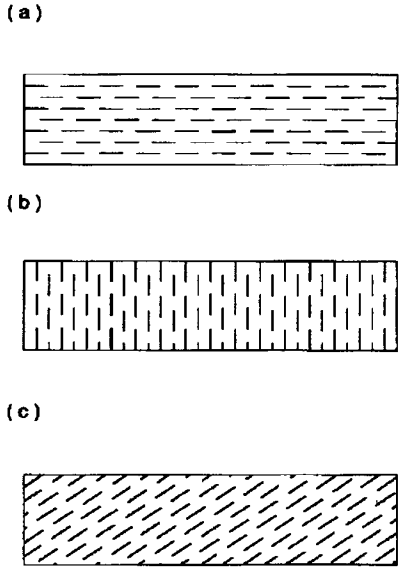
【図２】



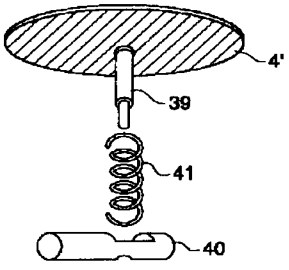
【図３】



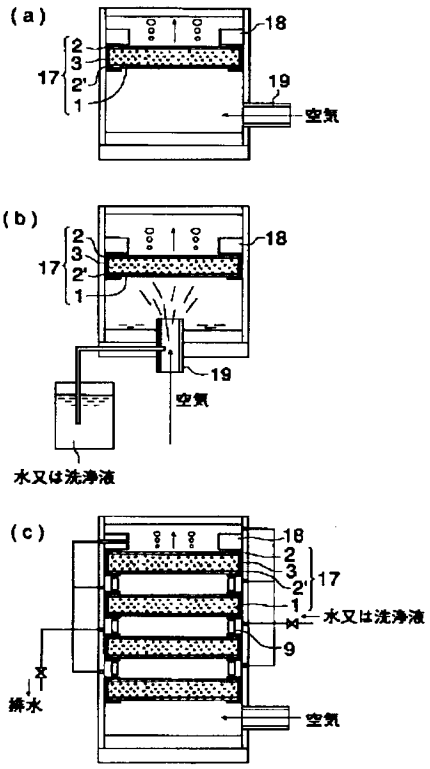
【図８】



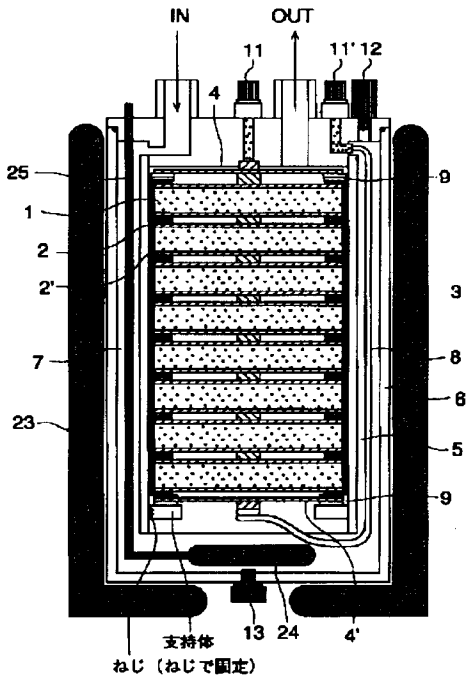
【図１３】



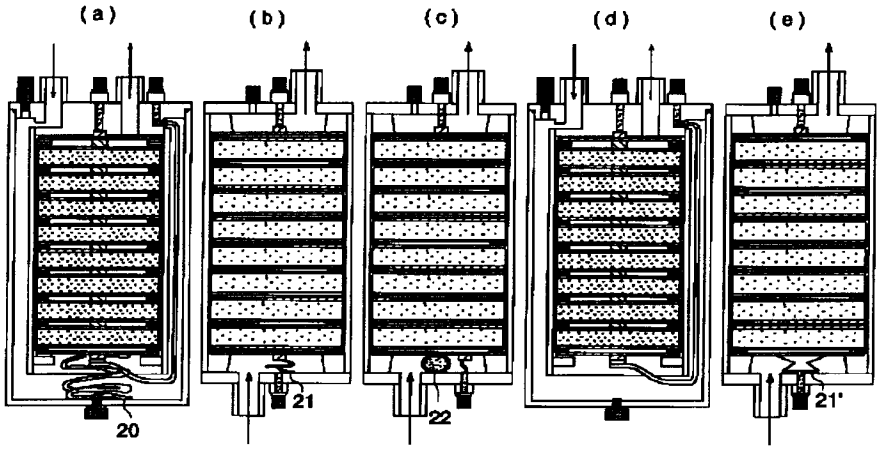
【図４】


(a)
18
2
3
17
2'
1
19
空気
(b)
18
2
3
17
2'
1
19
空気
水又は洗浄液
(c)
18
2
3
2'
17
1
水又は洗浄液
9
排水
空気

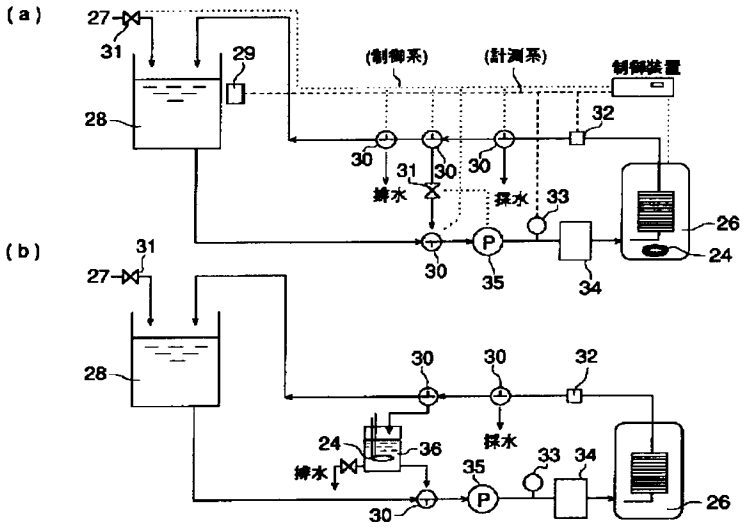
【図６】


IN
OUT
11
11'
12
4
25
9
1
2
2'
3
7
8
6
23
5
9
支持体
13
24
4'
ねじ（ねじで固定）

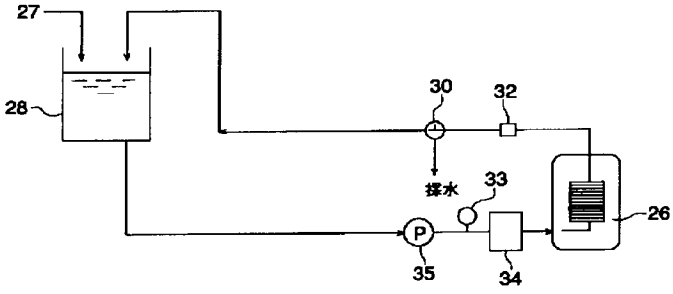
【図５】


(a)
(b)
(c)
(d)
(e)
20
21
22
21'

【図７】


(a)
27
31
29
28
(制御系)
(計測系)
制御装置
32
30
30
31
30
排水
採水
33
26
24
(b)
31
27
30
35
34
28
30
30
32
24
36
採水
排水
35
33
34
26
30

【図９】


27
28
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32
採水
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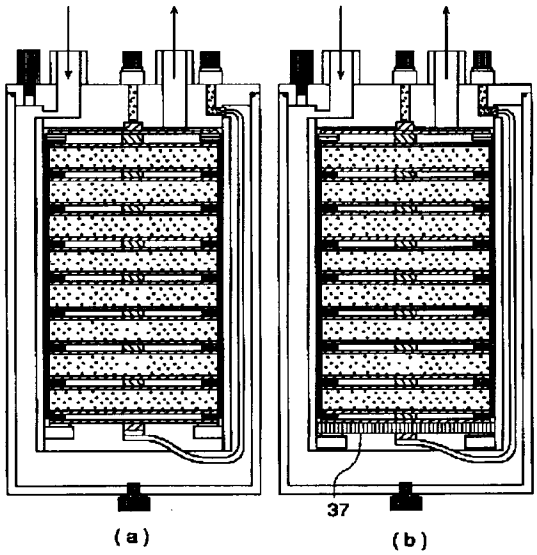
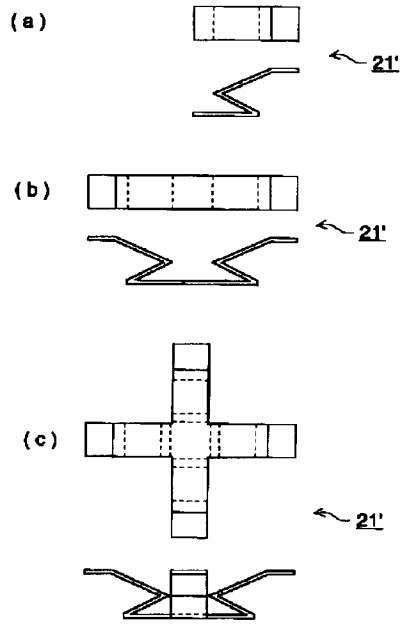
35
34

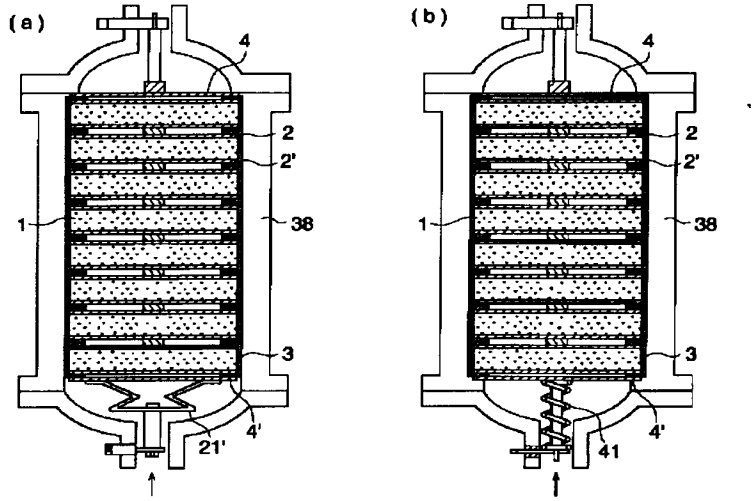
【図１０】


37
(a)
(b)

【図１１】



【図１２】



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